DARPA Palm Power: **Advanced Lithium Anodes for Li/Air & Li/Water Batteries**

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STATEMENT OF WORK

Abstract

PolyPlus Battery Company has developed glass protected lithium anodes that are chemically stable and electrochemically active in both aqueous and non-aqueous electrolyte. This innovation enables the development of both primary and secondary lithium batteries having exceptionally high gravimetric and volumetric energy densities. The gravimetric capacity of lithium is 3800 mAh/g and the open circuit potential for lithium/water and lithium/air couples is more than 3 volts, resulting in theoretical energy densities greater than 11,000 Wh/kg. The theoretical energy density for the Zn/air couple is about 900 Wh/kg, while practical cells are on the order of 300 Wh/kg (~ 30% of theo.). Assuming that engineering of the Li/air chemistry also results in practical cells having 30% of theoretical energy density, then one would predict practical batteries having greater than 3000 Wh/kg. This represents an order of magnitude improvement over existing commercial cells, and until recently thought to be attainable only using fuel cell technology. Accordingly, the following statement of work is targeted at defining the parameters of operation for glass protected lithium anodes. This information can then be used to project performance of protected Li anodes used in combination with existing air electrode technology for advanced Li/air batteries. If successful, a subsequent program will be launched to determine the actual performance of protected Li anodes in batteries having commercial and developmental air electrodes. The actual Li/air performance will then be projected into BA 5590 battery packs.

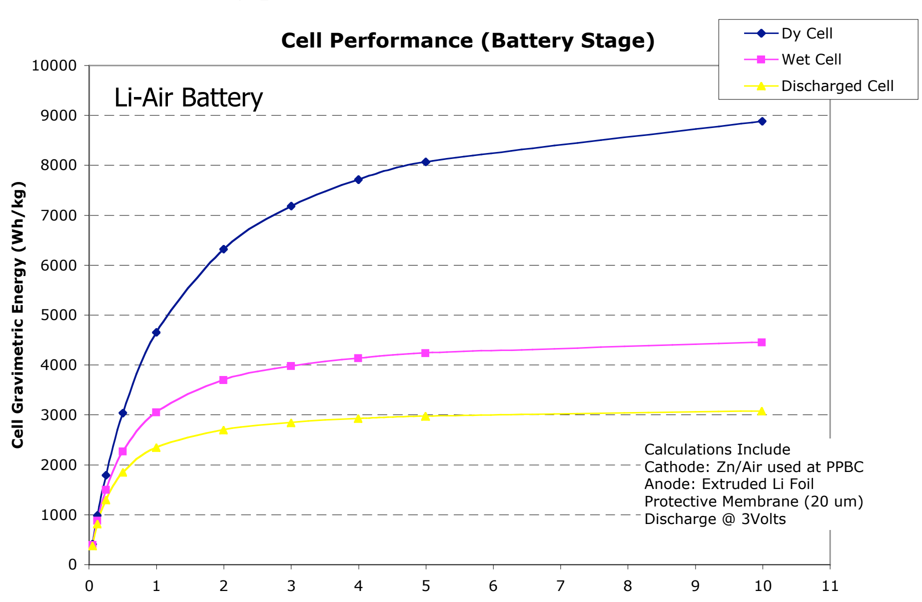

Figure 1. Specific Energy Projections for Li/air Battery

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Task 1. Half-cell design

The prime focus of this 6-month program is to define the performance of glass protected Li anodes for Li/aqueous battery chemistries. As such, in the first task an experimental cell will be designed where a variety of lithium foil thicknesses can be tested against a standard counter electrode in aqueous solutions. The experimental cell will consist of a glass protected Li foil of approximately 5 cm^2 active area, sealed against an aqueous electrolyte environment having a Ag/AgCl reference electrode and a Pt or Ni foam counter electrode. The cell body will most likely be made from borosilicate glass will o-ring and/or epoxy seals. PolyPlus has already built similar cells, and thus expects this task to be completed within two weeks of start of the contract.

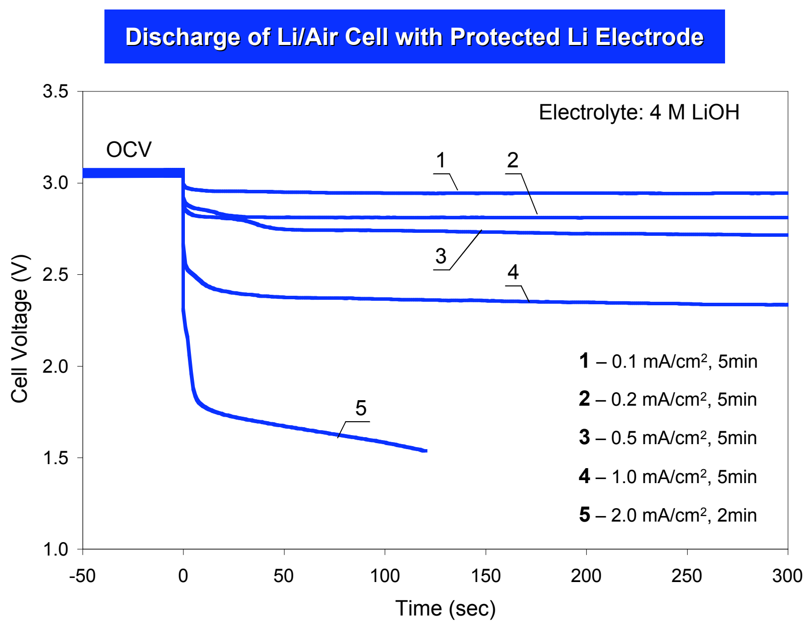

Figure 2. Preliminary testing of Li/air cell having protected Li anode

Task 2. Glass Protected Li anode performance

This is the most critical task for the 6-month program, and will continue for the duration of the program once the experimental cell is completed. The protected Li anodes will be characterized in terms of rate, lithium foil thickness, lithium purity, and temperature.

2.1 Capacity as a function of Lithium thickness (C_{max})

PolyPlus has tested Li anodes from 8 μm in thickness to 100 μm in thickness with no evidence of deterioration in performance. However, to achieve the exceptionally high energy densities possible with Li/air and Li/water, and to minimize electrode cost, it is desirable to increase the thickness of the Li metal electrode. In task 2 we will characterize the performance of the glass protected Li anode as a function of Li thickness. Thick protected Li anodes will be discharged to a voltage cutoff (vs. a Ag/AgCl ref.) in aqueous electrolytes to determine the anode degradation over time as a function of rate. Commercial foils of 1 to 3 mm in thickness will be bonded to the glass electrolyte and discharged to a pre-defined voltage cutoff. In the ideal scenario, the discharge profile will be flat over time, terminating with the depletion of the Li electrode capacity. In such a case, cell design will be a simple balance of energy density vs. power density desired. However, if the Li/glass interface degrades as a function of Li capacity, then the Li foil thickness may be limited to less than a critical thickness for electrode degradation. Li capacity will also be determined as a function of rate, ranging from 0.1 mA/cm^2 to 20 mA/cm^2.

2.2 Voltage drop as a function of electrolyte thickness – 300 µm, 100 µm, 50 µm, 20 µm

In this sub-task we will determine rate characteristics of the protected Li anode as a function of the glass electrolyte thickness. The ionic conductivity of the water stable glass is approximately 5×10^{-4} S/cm, yielding an ASR of 0.2 Ωcm^2/micron; a 50 µm film has an ASR of 10 Ωcm^2. Accordingly, if the voltage drop across the Li/glass membrane is purely ohmic, the voltage drop for a current density of 10 mA/cm^2 is only 100 mV. However, the current-potential characteristics of the Li/glass interface needs to be characterized systematically as a function of glass thickness. We have recently fabricated glass membranes of 50 µm in thickness, and these appear to be relatively flexible. Accordingly, we are exploring even thinner glass electrolytes for the Li/air and Li/water chemistries.

2.3 Rate characteristics – 0.3 mA/cm^2, 0.5 mA/cm^2, 1.0 mA/cm^2, 5 mA/cm^2, 10 mA/cm^2, 50 mA/cm^2

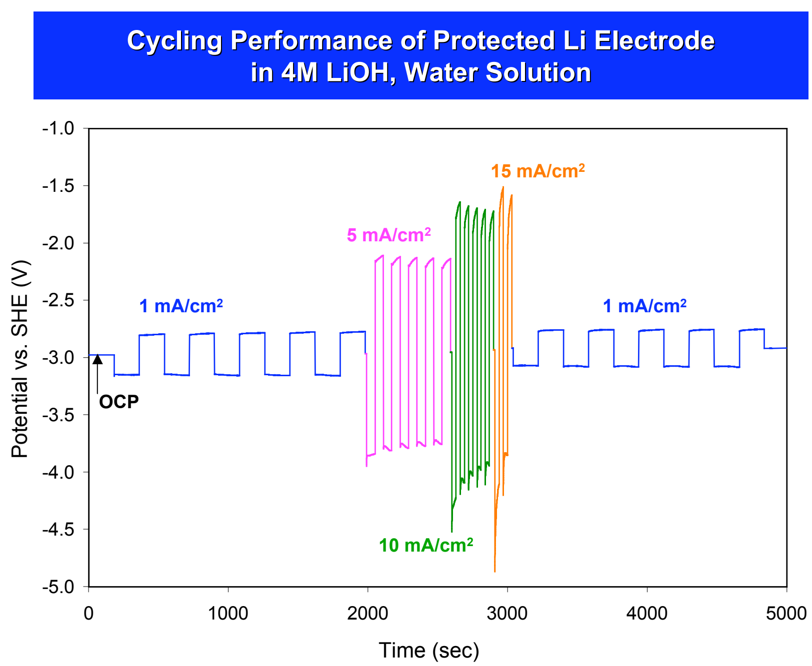

Figure 3. Initial high rate testing of protected Li anodes in aqueous solution

Zinc/air batteries can be discharged at high rates; the air electrodes can sustain rates as high as 50 to 100 mA/cm^2. Since the Li/air chemistry is about 3 volts (~ 1 volt for Zn/air), equivalent power densities will be achieved at current rates from 15 to 30 mA/cm^2. We have charge/discharge cycled Li/glass membranes at rates up to 15 mA/cm^2 with no evidence of deterioration in performance. However, these were shallow cycles, and more extensive testing of the rate capabilities of the Li/glass anodes is needed. High capacity protected Li anodes will be discharged to a coulomb cutoff at rates from 0.3 mA/cm^2 to 50 mA/cm^2 to determine anode performance as a function of rate. If continuous high rate discharge is achievable for Li/glass anodes, then it is highly likely that high power/high energy density Li/air cells will be commercialized, and deployed by both the U.S. military and in the global consumer marketplace.

2.4 Rate as a function of temperature -

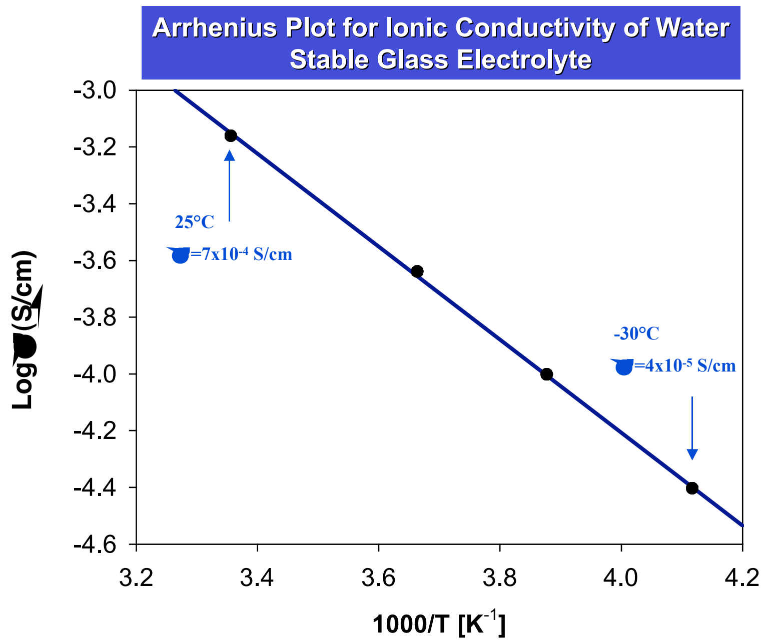

Figure 4. Conductivity of glass electrolyte as a function of temperature

The glass electrolyte used in the PolyPlus Li/glass technology is quite conductive at low temperatures; the Li ion conductivity at –30ºC is still 4 x 10^{-5} S/cm. Consequently we do not expect serious polarization of the Li/glass anode at low temperatures. In this task we will determine the performance of the Li/glass anode as a function of rate in aqueous electrolyte at temperatures down to –20ºC.

Task 3. Aqueous electrolyte cathodes for Li/air cells

The water-stable glass membrane (WSM) provides complete decoupling of the protected lithium anode from the cathode chemistry. This permits the combination of the PPBC lithium anode with any type of cathode, including acidic, neutral, or basic aqueous electrolytes. In the Lithium/Air variant, acidic or neutral cathode electrolytes are particularly appealing, since they avoid the uptake of the atmospheric carbon dioxide that limits the performance and shelf life of zinc/air and other metal/air chemistries. In task 3, the protected Li anode performance will be characterized in a variety of acidic, basic, and neutral aqueous electrolytes to determine the effect, if any, of pH on anode performance. The results will determine what modifications, if any, need to be considered for optimizing the air electrode structure and chemistry that lead to the most advantageous combination for support of the intended mission. If successful, a second phase program will evaluate commercial Zn/air cathodes (*e.g*. Rayovac Zn/Air, eVionyx, NREL, or other), that are subsequently filled with the cathode electrolyte of interest.

3.1 Acidic electrolytes:

Protected lithium anodes are tested in a variety of acids including hydrochloric, phosphoric, and sulfuric acid. The acidic electrolyte compositions tested in this evaluation phase are 0.5-5 molar acid with 0.5 to 1 molar LiCl as a supporting electrolyte. Higher acid molarities, compatible with commercial cathode materials may also be tried. The cell discharge leads to the formation of LiCl and evolution of H_2. Uptake of atmospheric CO_2 does not occur in such solutions. These tests will provide an estimate of the maximum amount of the Li salt product that can be accommodated in acidic electrolytes, polarization of the anode as a function of current density, and stability of the glass membrane in acid under dynamic and static conditions.

3.2 Neutral electrolytes:

The test cell configuration is identical to the one in Task 3.1. Electrolyte compositions include aqueous solutions of LiCl and NH_4Cl. For the ammonium chloride salt, the cell reaction for a lithium/air cell is:

$$Li + 1/2\ O_2 + NH_4Cl \Rightarrow LiCl + NH_3\uparrow$$

In this case, the cathode is essentially buffered, and CO_2 uptake is also avoided. The upper limit of the ammonium chloride concentration in the cathode is determined by its solubility limit, and by the current/capacity performance envelope of the cathode. Additionally, NH_4Br will evaluated, since it has a significantly higher solubility limit (~10 molar) compared to NH_4Cl (~5 molar).

3.3 Basic electrolytes:

The test cell configuration is also identical to the one described in Task 3.1. The electrolyte compositions in this case are aqueous solutions of LiOH in a concentration range between 0.5 and 5 molar. Cell discharge again leads to the release of hydrogen, as well as to the formation of more LiOH. In this case, however, atmospheric uptake of CO_2 cannot be avoided. These cells may have performance characteristics that may be different from those examined in Tasks 3.1 and 3.2, and would generally demonstrate the wide range of cathode electrolytes that can be contemplated.

Task 4. Li/Air & Li/Water Battery Projections

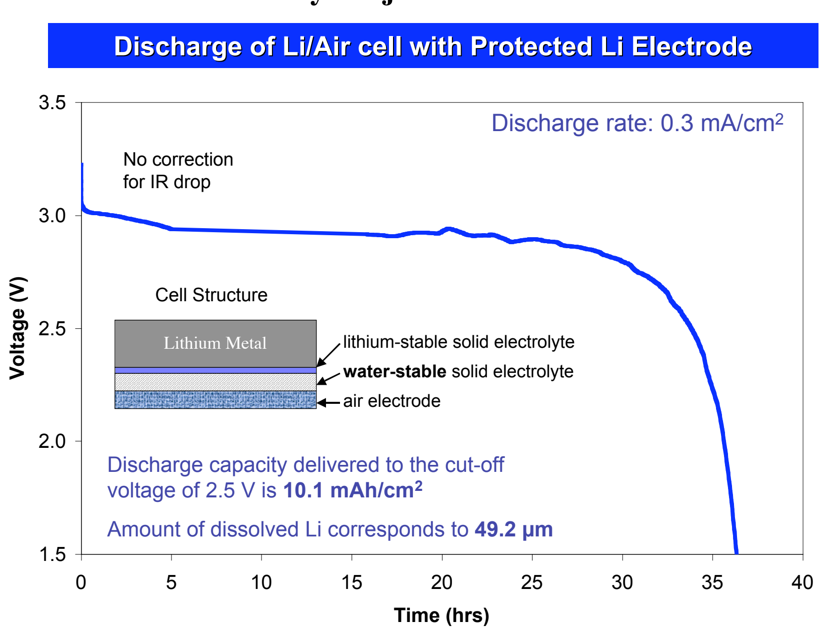

Figure 5. Extended discharge of Li/air with protected anode

The performance data acquired in tasks 2 and 3 will be used to project battery performance for a Li/air and/or Li/water equivalent to the BA 5590 battery. The performance data will be used as a guide to anode thickness considerations, and reasonable cell geometries will be used as a basis for estimating gravimetric and volumetric energy densities as well as power densities of Li/air batteries.

4.1 Li/Air estimates using various cathodes (Rayovac Zn/air, eVionyx, NREL, etc.)

Li/air cell projections will be made using data acquired in tasks 2 and 3, and data supplied by commercial developers of air electrodes such as Rayovac, eVionyx, and others. Ragone plots will be calculated for a variety of cell geometries and electrolyte compositions.

4.2 Li/Water

Ragone plots will also be calculated for Li/water cells based on the use of simple Ni foam cathodes. A variety of cell constructions will be considered including the possibility of using the Li/water cell as both a power source and a hydrogen generator for H_2/O_2 PEM cells.

4.3 Prismatic Li/Air to replace BA 5590

The results from task 4.1 will be used to project the performance of an equivalent Li/air battery pack as a replacement for the BA 5590 battery. It is anticipated that the specific energy for the Li/air pack will exceed 1000 Wh/kg, and depending on packaging, may be significantly higher.

SCHEDULING

Advanced Li anodes	WBS	Start Date	Finish Date
Half-cell Design	1	4/1/04	4/15/04
Li anode performance	2	4/15/04	9/15/04
Anode capacity as a fcn of Li thickness	2.1	4/15/04	7/30/04
Effect of glass thickness	2.2	5/3/04	6/30/04
Rate characteristics	2.3	6/16/04	8/31/04
Rate as a fcn of temperature	2.4	8/2/04	9/15/04
Aqueous electrolytes for Li/air	3	6/1/04	8/31/04
Acidic electrolytes	3.1	6/1/04	6/30/04
Neutral electrolytes	3.2	7/1/04	7/30/04
Basic electrolytes	3.3	8/2/04	8/31/04
Li/air & Li/water projections	4	9/1/04	9/30/04
Li/air estimates	4.1	9/1/04	9/24/04
Li/water estimates	4.2	9/1/04	9/15/04
BA 5590 projection	4.3	9/30/04	
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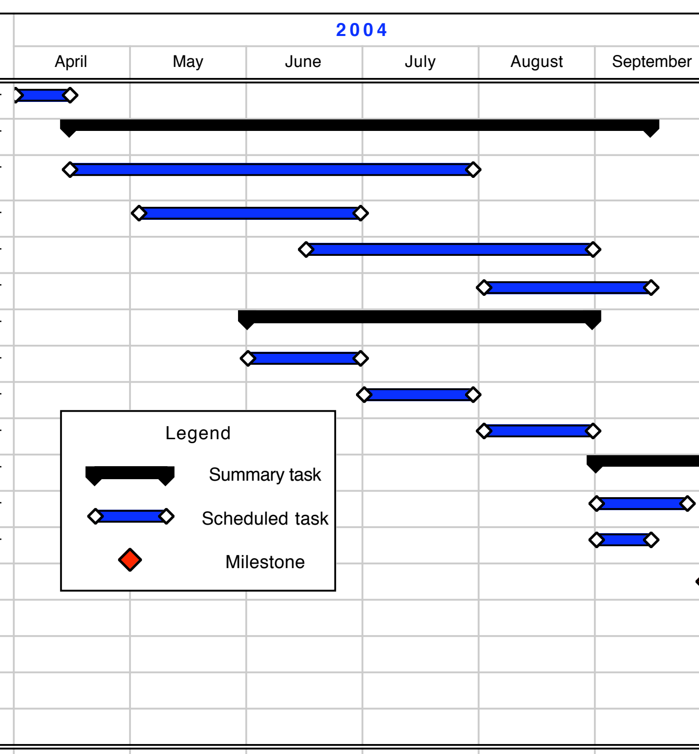


BUDGET

The anticipated budget for this 6-month program is $750k. A detailed budget will be submitted with the full proposal.

Defense Advanced Research Projects Agency
Defense Sciences Office

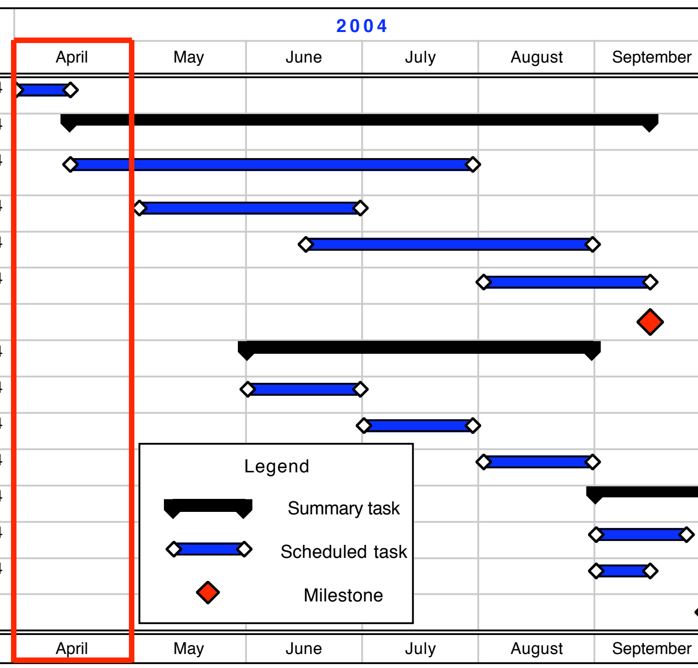
Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company April 2004 Report

Technical Highlights

Scheduled tasks: In the 1st contract month, key tasks involved design and construction of a half-cell for determination of Li anode performance, and initial tests of anode capacity as a function of lithium metal thickness; both of these tasks were completed as scheduled and are described below. Notably, PolyPlus demonstrated a **coulombic efficiency of at least 99%** for a lithium foil of 100 μm in thickness discharged at 0.3 mA/cm^2 in seawater.

Advanced Li anodes	WBS	Start Date	Finish Date
Half-cell Design	1	4/1/04	4/15/04
Li anode performance	2	4/15/04	9/15/04
Anode capacity as a fcn of Li thickness	2.1	4/15/04	7/30/04
Effect of glass thickness	2.2	5/3/04	6/30/04
Rate characteristics	2.3	6/16/04	8/31/04
Rate as a fcn of temperature	2.4	8/2/04	9/15/04
Anode defined	2.5	9/15/04	
Aqueous electrolytes for Li/air	3	6/1/04	8/31/04
Acidic electrolytes	3.1	6/1/04	6/30/04
Neutral electrolytes	3.2	7/1/04	7/30/04
Basic electrolytes	3.3	8/2/04	8/31/04
Li/air & Li/water projections	4	9/1/04	9/30/04
Li/air estimates	4.1	9/1/04	9/24/04
Li/water estimates	4.2	9/1/04	9/15/04
BA 5590 projection	4.3	9/30/04	



Task 1: Half-cell design

An experimental cell for testing a variety of Li foil thicknesses in aqueous electrolytes was designed. The cell shown in Fig. 1 contains an anode compartment with a glass protected Li foil of 2.0 cm^2 active area on a Cu substrate sealed against an aqueous solution such that only the protective glass membrane is exposed to an aqueous environment, a reference electrode, and a metal screen counter electrode. The cell body made from the borosilicate glass is filled with approximately 50-250 ml of the electrolyte depending on the position (depth) of the protected anode immersed in the electrolyte. The metal screen counter electrode is used as a cathode to facilitate hydrogen evolution (water reduction) during Li anodic dissolution. The Ag/AgCl reference electrode placed next to the surface of the protective glass membrane is used to control potential of the Li anode during discharge. Measured values were recalculated as potentials in the Standard Hydrogen Electrode (SHE) scale. The cell is equipped with a vent to release hydrogen gas generated on the cathode.

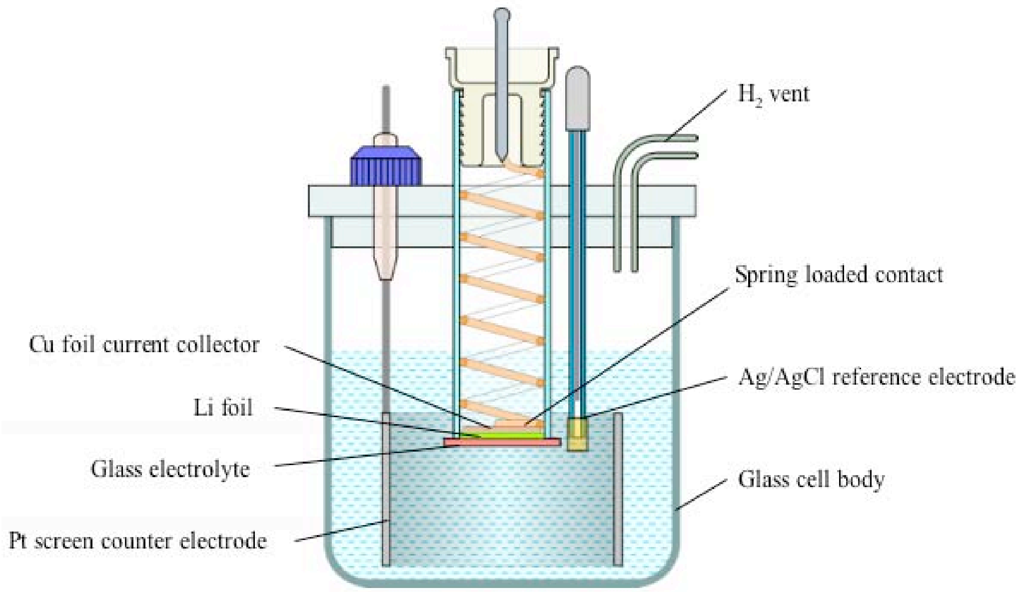


Figure 1. Experimental Cell Design

Task 2: Glass Protected Li anode performance

2.1 Capacity as a function of lithium thickness.

Experiments with thick foils-Li anode fabrication:

In order to achieve the very high energy densities possible with Li/air and Li/water systems it is desirable to use thick Li electrodes. PolyPlus ordered and received Li foils with thicknesses of 0.6 and 1.0 mm made by FMC Corporation as a special order. These foils can be directly used for fabrication of glass protected anodes and in the experiments on Li stripping. However, as one can see from Table 1, the capacity of these foils can be too small to achieve the required time of discharge especially at moderate current rates.

PolyPlus developed a method for fabricating thicker Li foils on Cu substrates using static pressing of two or more foils with thicknesses of 0.6 or 1.0 millimeters. Under normal conditions Li foil is always covered with a native passivation film consisting of a variety of lithium compounds, in particular Li oxide and Li carbonate. The process of lamination of two Li foils developed at PolyPlus included activation of the Li surface and static pressing of two foils together. PolyPlus showed that removal of the native film from the Li surface by polishing the surface with a Tyvec fabric just before pressing led to a significant increase in Li surface adhesion during Li foil lamination. Optimization of pressing and polishing conditions allowed us to fabricate Li foils with thicknesses of approximately 1.5-1.7 millimeters attached to the Cu foil substrates. PolyPlus is currently working on processing of thicker Li foils (3 millimeters and thicker). Predicted discharge capacities for Li foils of up to 3 millimeters in thickness are presented in Table 1.

Table 1. Calculated capacities and discharge times for various Li foil thicknesses

Li foil thickness, mm	Li foil capacity, mAh/cm^2	Time of discharge at various rates, days		
		$0.3\ mA/cm^2$	$0.5\ mA/cm^2$	$1.0\ mA/cm^2$
0.6	123	17	10	5
1.0	205	28	17	9
1.5	307	43	26	13
3.0	615	85	51	26

Fabrication of glass protected Li anode for initial testing:

For initial testing of glass protected Li electrode performance we used a commercial Li foil (~110 µm thick) from Chemetall Foote Corp. The Li foil was pressed onto 25 µm Cu foil substrate and then mechanically bonded to the protective glass membrane. The surface of Li was polished with a Tyvec fabric just before mechanical bonding. A Carver hydraulic press located in the dry room was used for the pressing operations. The applied pressure was around 800 kg/cm^2, and the time of pressing was 10 minutes. In these initial experiments the glass electrolyte had a thickness of 480 µm.

Electrolyte composition and properties:

For initial experiments on discharge of protected Li foils PolyPlus used cells containing seawater as an electrolyte. The artificial seawater was prepared with 35 ppt of "Instant Ocean" salt from Aquarium Systems, Inc. dissolved in deionized water. The composition of the salt provided by the manufacturer, is presented in Table2. The electrolyte was characterized at PolyPlus. The conductivity of the solution was determined to be 4.5×10^{-2} S/cm, and the solution's pH was 8.7. A Pt screen was used as a cathode for electrochemical hydrogen evolution from the seawater electrolyte.

Table 2. Composition of "Instant Ocean" salt used for electrolyte preparation

pH	**8.78 (PPBC data)**
Chloride	19,154 ppm
Sodium	10,637 ppm
Sulfate	2,684 ppm
Magnesium	1,273 ppm
Calcium	372 ppm
Potassium	428 ppm
Bromide	5.4 ppm
Strontium	6.87 ppm
Silicate	1.80 ppm
Phosphate	<0.003 ppm

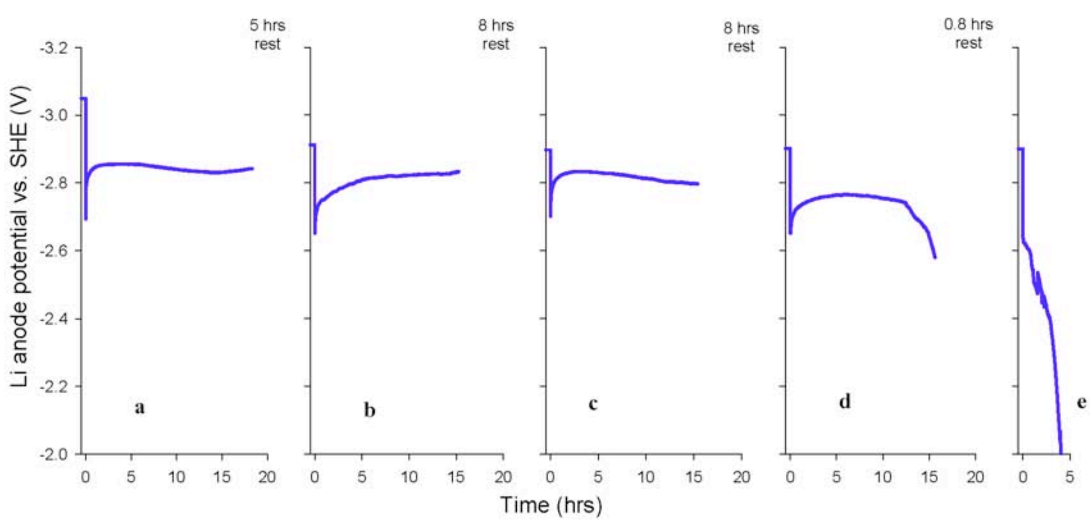
RESULTS OF ELECTROCHEMICAL TESTS.

Once the protected Li anode was immersed in the electrolyte, no evidence of reaction, in particular Li dissolution or gas evolution at the anode was seen. Remarkably, an open circuit potential (OCP) of 3.05 volts corresponding closely to the thermodynamic potential difference between Li/Li^+ and H_2/H^+ in water was observed. Without Li protection, one could not observe this potential due to a significant shift of the Li electrode potential in the positive direction caused by extremely intensive corrosion of lithium metal in seawater (over 19,000 mA/cm^2 (Shuster, 1990)). When the circuit was closed, hydrogen evolution was seen only at the Pt cathode surface. This is the first known example of a lithium/water battery operated in the absence of very large corrosion currents.

The potential-time curves for anodic dissolution of protected Li anode are presented on Fig. 2. The test procedure included several partial discharges at a current density of 0.3 mA/cm2. Each discharge was followed by several hours of rest under OCV conditions. The cell temperature ranged from 23 to 29°C, and was allowed to vary naturally.

The cell exhibited a long discharge with a high average discharge voltage of approximately 2.8 V. Discharge capacity delivered to the cut-off voltage of 2.0 V was close to 21 mAh/cm^2. This Li capacity value corresponds to a Li thickness of 101 μm. The measured thickness of Li foil from Chemetall Foote Corp. after pressing onto the Cu substrate was in the range of 101 to 103 μm. Postmortem analysis of the Li electrode confirmed that after Li anodic dissolution only very small islands of Li residue were left on the Cu substrate. Therefore, over 100 μm of Li were completely stripped from the inert Cu substrate and moved through the Li anode/aqueous electrolyte interface without destruction of the glass protective layer.

Fig.2 Partial Discharges for Glass Protected Li Anode at Current Density of 0.3 mA/cm^2



Total discharge time of 69.1 hrs corresponds to the thickness of dissolved Li of 101 micrometers

Rest after partial discharges: 5 hrs after discharge **a**

8 hrs after discharge **b**

8 hrs after discharge **c**

0.8 hrs after discharge **d**

Defense Advanced Research Projects Agency
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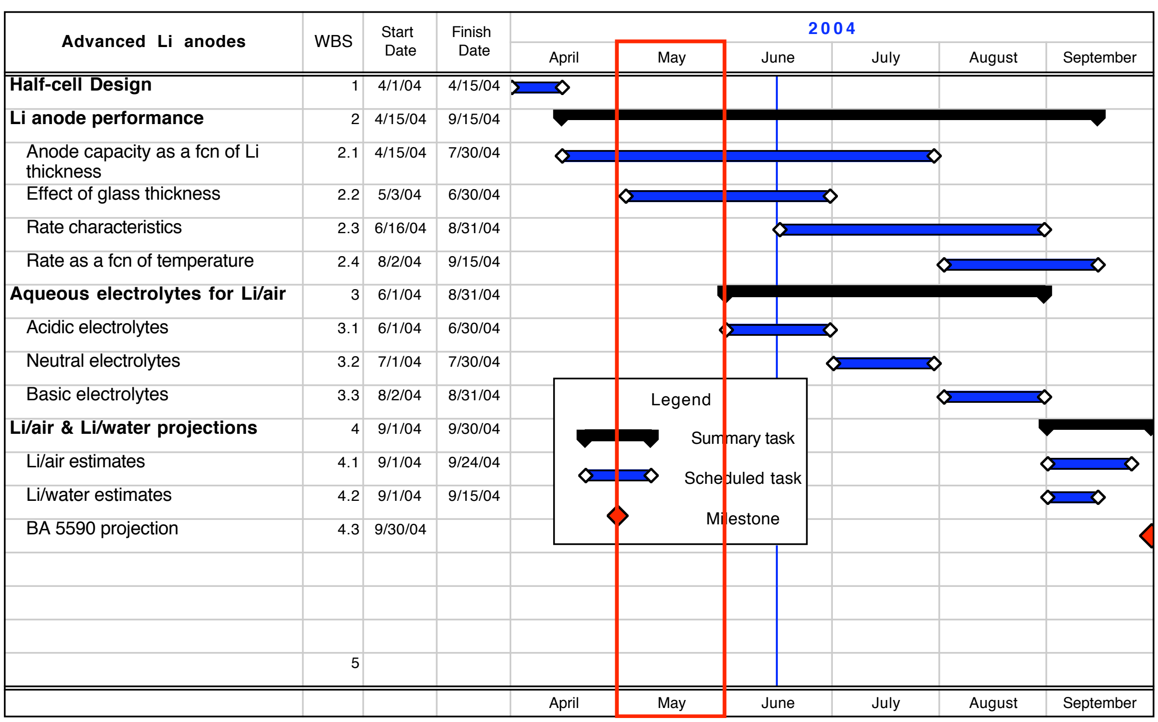
Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company May 2004 Report

Technical Highlights

Scheduled tasks: In the second contract month, key tasks involved tests of anode capacity as a function of Li metal thickness and determination of the Li anode polarization as a function of protective glass thickness. Both of these tasks were completed as scheduled and the data are described below. PolyPlus achieved discharge of about 735 micrometers of Li through the protective glass at 0.5 mA/cm^2 in acidic electrolyte. Notably, initial experiments show that a Li anode protected with a 100 µm solid electrolyte membrane exhibits significantly smaller anodic polarization than its counterpart having 320 µm thick membrane.

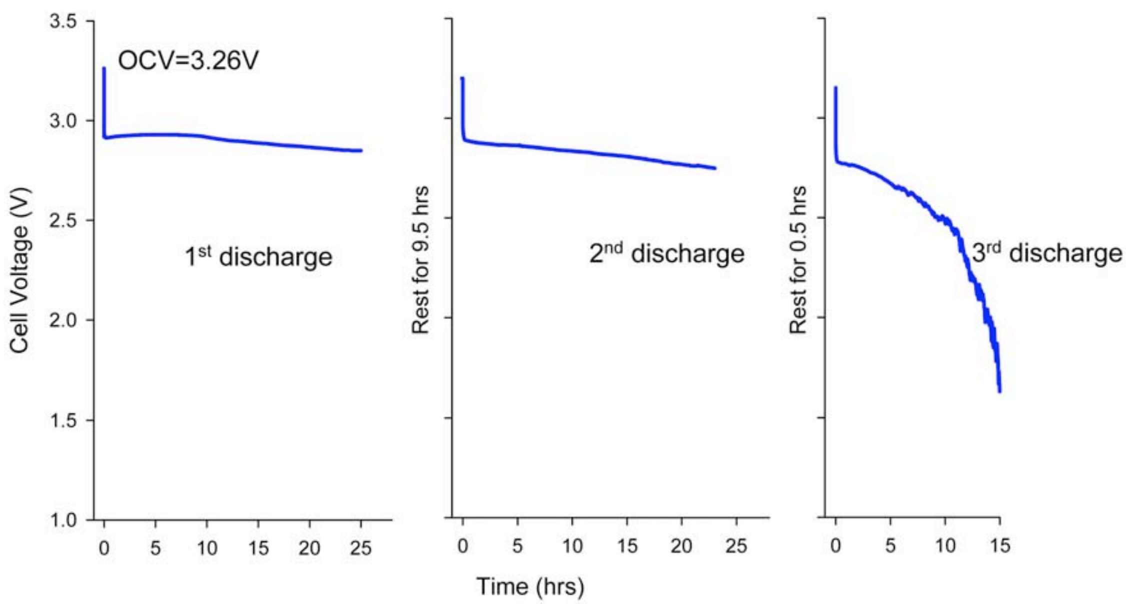


Task 2: Glass Protected Li anode performance

<u>2.1 Capacity as a function of lithium thickness</u>.

Electrochemical testing of Li foils with moderate thickness in Li/air cells:

In the PolyPlus April 2004 report we showed that for a Li/seawater cell, more than 100 µm of Li could be discharged across the solid electrolyte membrane. In response to teleconference discussions, PolyPlus has also initiated long term testing of Li/Air cells. In this case we used an electrolyte containing 1 M LiOH and an air cathode developed for Zn/air batteries. The thickness of the protective glass was 300 µm, and the thickness of the Li foil on a Cu substrate was in the range of 150-160 µm. The Li/air cell was discharged for a total of 63 hrs at a current density of 0.5 mA/cm^2 (See Fig. 1). After an initial 25 hour discharge, the Li/Air cell was rested at open circuit potential for 9.5 hrs without affecting the shape of the subsequent discharge curve. Due to the protective nature of the glass membrane, no corrosion of the lithium occurred during the 10 hour (9.5 + 0.5) rests at open circuit, and the entire 154 µm of lithium was discharged at the completion of the 3rd discharge.



Total discharge time of 63.2 hrs corresponds to the thickness of discharged Li of 154 µm

Figure 1. Intermittent discharge of Li/Air cell with solid electrolyte protected Li anode at a current density of 0.5 mA/cm^2 (9.5 hour rest after initial discharge)

Experiments with thick foils-Li anode fabrication:

In order to achieve the very high energy densities possible with Li/air and Li/water systems, fairly thick Li metal electrodes have to be used in the cell construction. In the April 2004 report we described a method for fabricating Li foils with thicknesses of up to 1.5-1.7mm on Cu substrates based on static pressing of two or more free-standing foils with thicknesses of 0.6 or 1.0 mm received from FMC Corporation. However, some military applications may require the use of even thicker Li foils. Calculated discharge capacities for Li foils of up to 6.0 millimeters in thickness and the duration in days of Li dissolution at various current densities are presented in Table 1. Suppliers of lithium metal foils in the U.S. do not routinely produce such thick multi-millimeter foils. In addition, the Li foils need to be bonded to an inert metal current collector. Accordingly, PolyPlus had to devise a scheme to produce such foils in-house.

One approach involves the cold lamination of thinner foils to produce a thick Li electrode. Among the difficulties of the lamination process is the need to remove the native film on lithium to allow bonding. Consequently, PolyPlus has developed an alternative method for fabricating a variety of thick Li electrodes on Ni substrates suitable for use in cells with aqueous electrolytes (figure 2).

Table 1. Calculated capacities and durations of discharge for various Li foil thicknesses

Li foil thickness, mm	Li foil capacity, mAh/cm^2	Time of discharge at various rates, days		
		0.5 mA/cm^2	1.0 mA/cm^2	10.0 mA/cm^2
1.5	307	26	13	1.3
3.0	614	51	26	2.6
4.5	921	77	38	3.8
6.0	1228	102	51	5.1

The PolyPlus technique for producing thick electrodes is illustrated schematically in Figure 2. This process relies on cold extrusion and rolling of Li foil (multi-pass for thinner foils), followed by static pressing of the Li foil onto the rough surface of the Ni current collector with a hydraulic press. A special die with a polypropylene body was designed and fabricated for the pressing operation to avoid chemical reaction with the lithium foils.

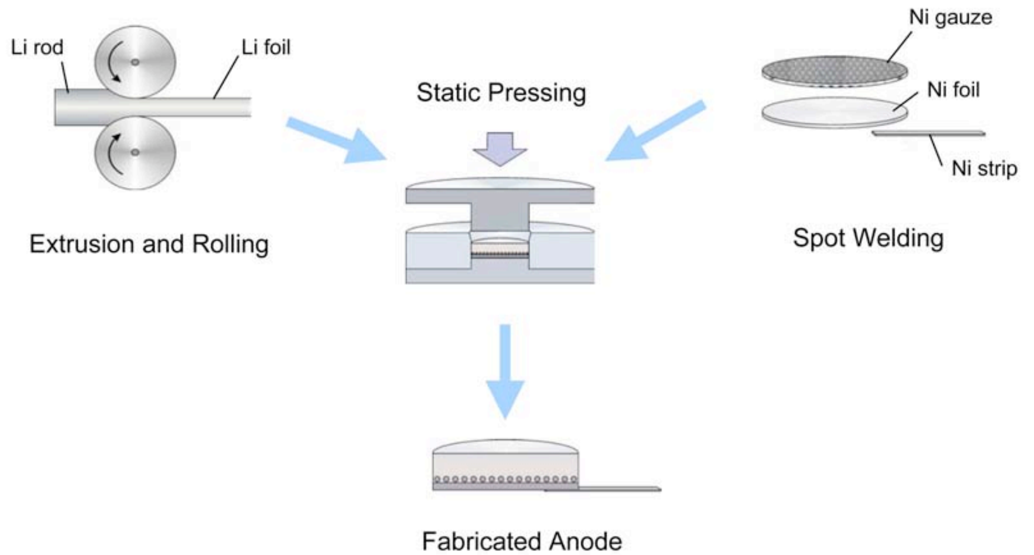


Figure 2. Fabrication of thick lithium anodes on nickel substrates

Aqueous electrolytes:

For experiments on the discharge of protected Li foils in Li/Aqueous half-cells we used acidic electrolytes based on H_3PO_4 or HCl (with LiCl salt), as well as a neutral electrolyte containing NH_4Cl. A Ti screen was used as the cathode for electrochemical hydrogen evolution from the acidic or neutral electrolytes.

Results of electrochemical testing of thick Li anodes in Li/water cells:

<u>HCl based electrolyte</u>

The potential-time curve for continuous discharge of protected Li anode in an aqueous solution of 1 M HCl, 2 M LiCl is presented on Fig. 3. This cell exhibited a long discharge at a closed circuit voltage of approximately 2.65-2.80V. The cell temperature was allowed to vary naturally during this experiment, with the difference between day and night temperatures being as large as 6-7˚C.[1] Oscillations in the potential-time curve reflect changes in the resistance of the thick protective glass with temperature.

In this experiment we increased the current density from that shown in the April report (0.3 mA/cm^2) to 0.5 mA/cm^2 and yet the value of achieved discharge capacity was significantly larger: about **735 µm of lithium** was moved across the Li anode/aqueous electrolyte interface without destruction of the glass protective layer. Electrochemical experiments on anodic dissolution of even thicker Li anodes in HCl based electrolytes will be continued in June 2004.

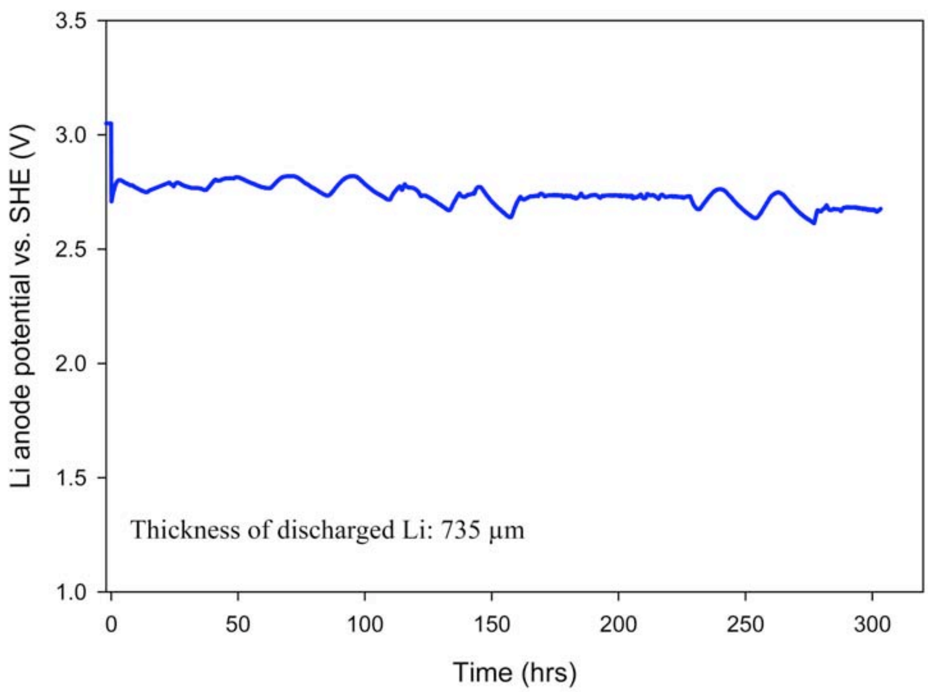


Figure 3. Discharge of thick protected Li in 1 M HCl, 2 M LiCl electrolyte at 0.5 mA/cm^2

<u>H_3PO_4 based electrolyte:</u>

The potential-time discharge curve obtained for a glass protected Li anode in a 1 M solution of H_3PO_4 is shown in Figure 4. At a current density of 1.0 mA/cm^2 the Li electrode in the cell with phosphoric acid electrolyte exhibited a discharge plateau at approximately 2.6-2.7 volts (vs. SHE) followed by a sudden drop in potential. Total discharge capacity corresponded to the dissolved Li thickness of 445 µm. Postmortem

[1] In all experiments on Li discharge described below the cells were kept at 25º C

analysis of the cell after discharge showed that the surface of the glass membrane was etched in the phosphoric acid and cracked. This is not entirely surprising, as phosphoric acid is known to etch ceramic materials. Accordingly, PolyPlus has initiated studies of long-term stability of the glass membranes in a variety of acidic, basic, and neutral aqueous electrolytes.

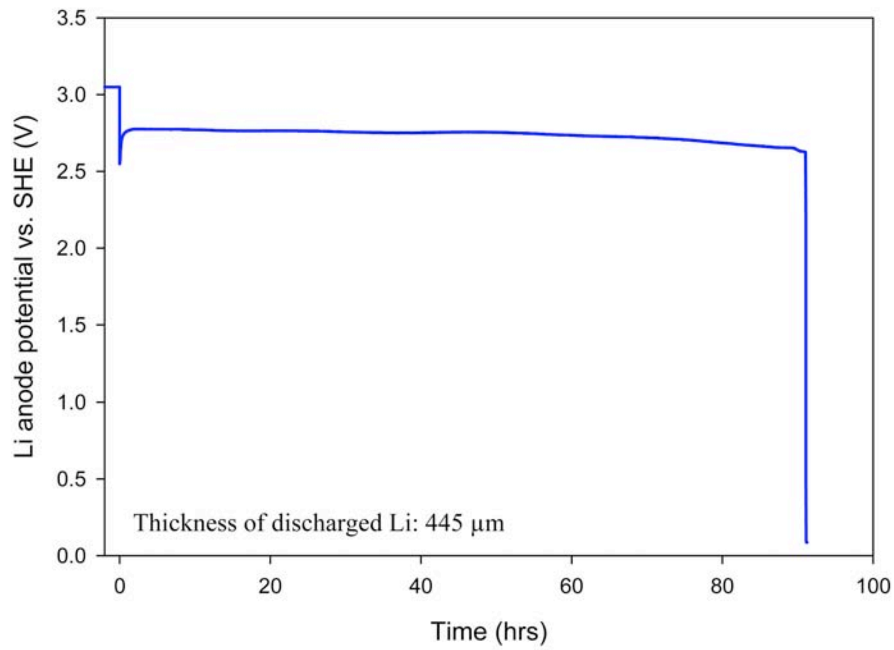
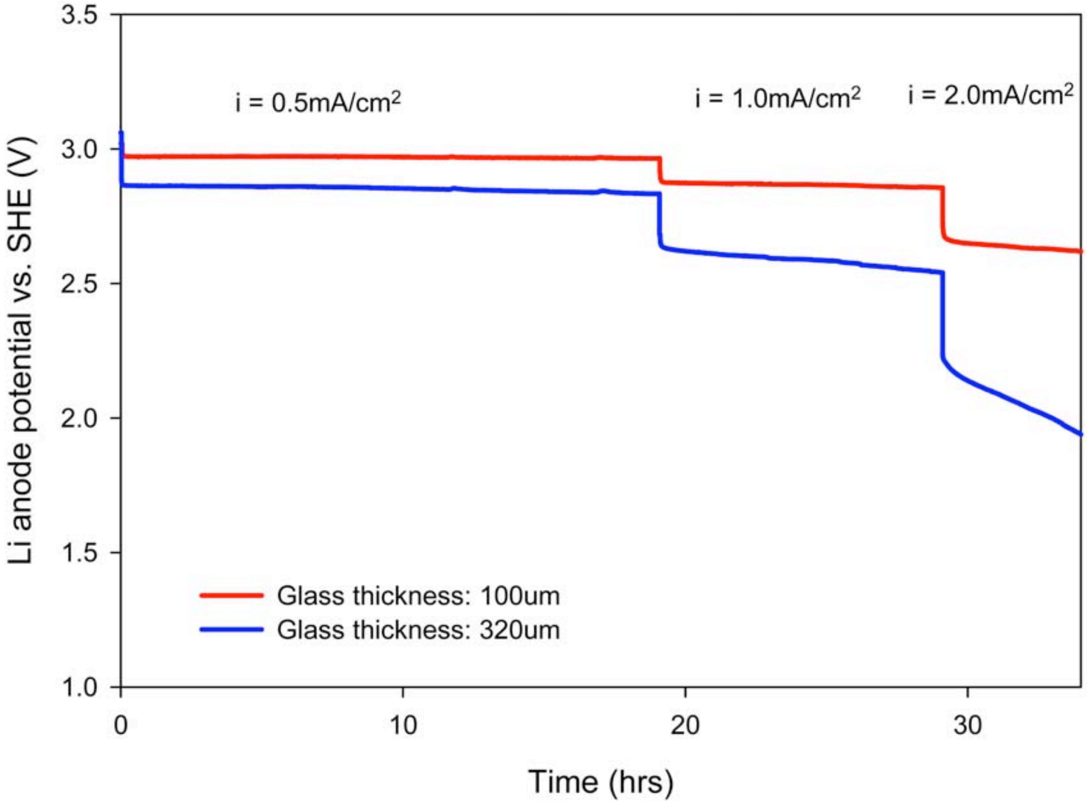


Figure 4. Discharge of solid electrolyte protected Li anode in 1 M H_3PO_4 at 1.0 mA/cm^2

2.1 Effect of glass thickness

The aim of this sub-task is to determine the effect of protective glass thickness on Li electrode polarization. In the experiments described below we used various discharge rates and, therefore, started working on the next sub-task related to rate characteristics of the protected anode.

For this study we chose 3.5 mm thick Li electrodes protected with glass membranes of two different thicknesses: 100 μm and 320 μm. The aqueous electrolyte contained 4 M NH_4Cl and was able to buffer the cathode during discharge. The fabricated Li/water cells were sequentially discharged at current densities of 0.5, 1.0 and 2.0 mA/cm^2 for 20, 10 and 5 hrs respectively. The capacity delivered at each step of discharge was the same and corresponded to discharge of 50 μm of Li. As one would expect, the value of the Li electrode polarization is larger with increasing current density. The Li anode protected with a 100 μm thick glass membrane exhibited significantly smaller anodic polarization than its counterpart having glass with a thickness of 320 μm. Remarkably, for these two anodes the difference in polarization values determined just after applying current steps of various amplitude (0.5, 1.0 and 2.0 mA/cm^2) corresponds to the difference in the resistances for the thin and thick glass membranes, implying that performance of the protected Li anodes will improve significantly as the thickness of the glass membrane is reduced. As indicated in the Gantt chart on page 1, investigation of the effect of glass thickness on performance of the Li anode at various discharge rates will be continue in detail during June 2004.



Each step of discharge corresponds to 50µm of dissolved Li

Figure 5. Sequential discharge of lithium electrode with 2 different thicknesses of solid electrolyte membrane at 0.5 mA/cm^2, 1.0 mA/cm^2, and 2.0 mA/cm^2

Defense Advanced Research Projects Agency
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Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company June 2004 Report

Technical Highlights

Scheduled tasks: In the third contract month, key tasks involved determination of the Li anode polarization as a function of glass membrane thickness and tests of anode capacity as a function of Li metal thickness in acidic electrolytes. Both of these tasks were completed as scheduled and the data are described below. PolyPlus achieved discharge of approximately 1.4 mm of Li through the protective glass in acidic electrolyte. Our experiments show that the anode protected with a 50 µm thick glass electrolyte membrane has quite an acceptable anodic polarization at moderate current rates.

Advanced Li anodes	WBS	Start Date	Finish Date
Half-cell Design	1	4/1/04	4/15/04
Li anode performance	2	4/15/04	9/15/04
Anode capacity as a fcn of Li thickness	2.1	4/15/04	7/30/04
Effect of glass thickness	2.2	5/3/04	6/30/04
Rate characteristics	2.3	6/16/04	8/31/04
Rate as a fcn of temperature	2.4	8/2/04	9/15/04
Aqueous electrolytes for Li/air	3	6/1/04	8/31/04
Acidic electrolytes	3.1	6/1/04	6/30/04
Neutral electrolytes	3.2	7/1/04	7/30/04
Basic electrolytes	3.3	8/2/04	8/31/04
Li/air & Li/water projections	4	9/1/04	9/30/04
Li/air estimates	4.1	9/1/04	9/24/04
Li/water estimates	4.2	9/1/04	9/15/04
BA 5590 projection	4.3	9/30/04	
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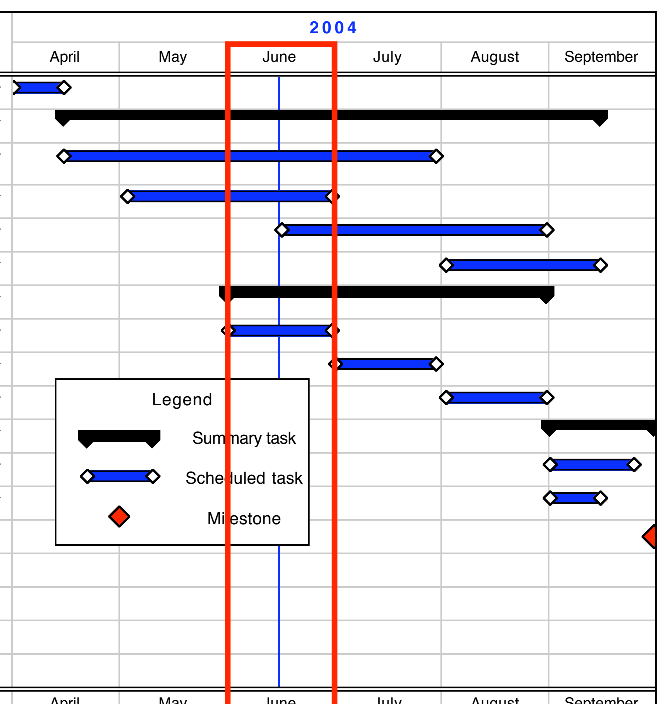

Task 2: Glass Protected Li anode performance

Preliminary battery specifications for PolyPlus project require a power of 30 W and an open circuit voltage of 19.2 V. We performed calculations of Li anode thicknesses at various current densities for a battery having 30 W power and 20 V discharge voltage.

The data are presented in Table 1.

Table 1. Parameters of Li anode for Li / Air Battery

Mission duration, days	Capacity, mAh	Current Density, mA/cm^2	Required Li Surface Area, cm^2	Required Li thickness, µm
1.0	36,000	1.0	1500	117
		2.0	750	234
		5.0	300	585
		10.0	150	1171
3.0	108,000	1.0	1500	352
		2.0	750	702
		5.0	300	1755
		10.0	150	3520

As one can see from this table, a one-day mission requires only 117 µm of Li at a current density of 1.0 mA/cm^2 and almost 1.2 mm of Li at 10 mA/cm^2. Accordingly, a three-day mission requires 352 µm of Li at 1.0 mA/cm^2 and more than 3.5 mm of Li at 10 mA/cm^2.

2.1 Capacity as a function of lithium thickness.

Fabrication of thick Li foils:

In order to achieve the parameters of Li/air battery listed in Table 1, Li electrodes have to be quite thick. For producing Li electrodes with a thickness of 3.0-3.5 mm we used the method developed at PolyPlus and described in the May 2004 report. The technique involves cold extrusion and rolling of Li foil followed by static pressing of the Li foil onto the surface of the Ni current collector with a hydraulic press in a special die having a polypropylene body.

Aqueous electrolyte:

For experiments on the discharge of protected Li foils in Li/Water cells we used an electrolyte based on NH_4Cl, which is slightly acidic before Li discharge, or a neutral electrolyte containing LiCl. A Ti screen was used to facilitate electrochemical evolution of hydrogen on a cathode surface.

Results of electrochemical testing of thick Li anodes in Li/water cells:

NH_4Cl based electrolyte, standard composition of glass membrane

The potential-time curve for continuous discharge of protected Li anode in aqueous solution of 4 M NH_4Cl is shown on Fig. 1. The cell exhibited a long discharge with a discharge voltage of approximately 2.65-2.75 V. The value of achieved discharge capacity was very large. Approximately **1.4 mm of Li** was moved across the Li anode/aqueous electrolyte interface without destruction of the glass protective layer. The value of Li discharge capacity in this experiment is significantly larger than a Li thickness of 735 µm reported in the May 2004 report for glass protected Li in the acidic solution (1 M HCl, 2 M LiCl in water). Notably, this result is achieved for a practically important aqueous electrolyte system containing NH_4Cl, which can buffer the cathode and prevent electrolyte carbonization during cell storage and discharge.

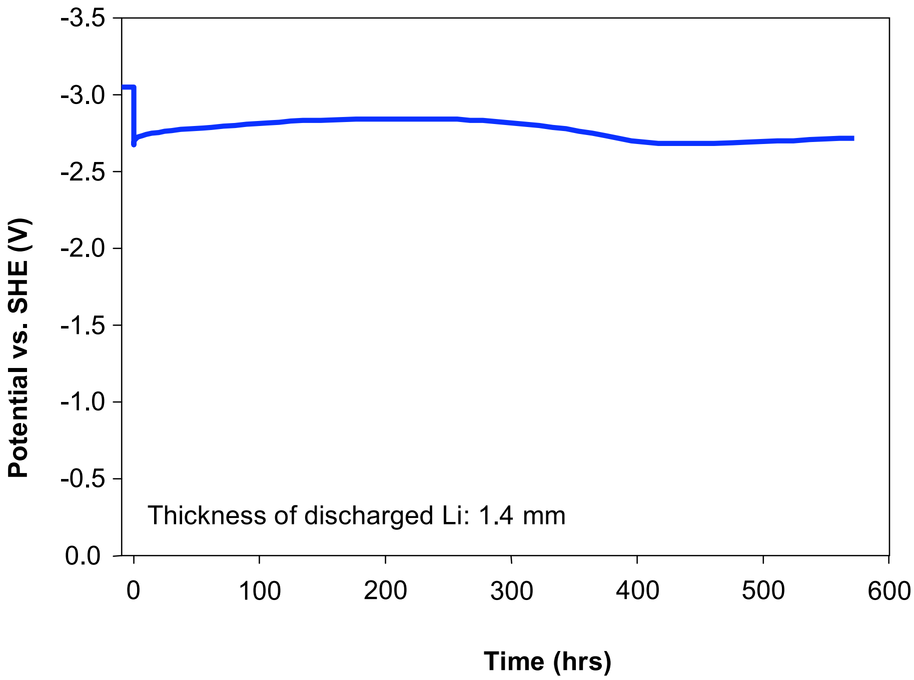

Figure 1. Discharge of thick protected Li in 4M NH_4Cl aqueous electrolyte at 0.5 mA/cm.

<u>NH_4Cl based electrolyte, new composition of glass membrane</u>

In this experiment we used a glass membrane of 300 µm thickness with a modified composition. This glass is expected to be more stable to reduction than the standard glass used in all of our previous experiments. More importantly, this glass has much improved mechanical properties and is easier to produce in the form of large thin sheets using commercial draw-down techniques (experiments in progress).

One of the main parameters of the glass membrane is the value of its ionic conductivity which affects battery power and energy densities. We performed measurements of ionic conductivity of the glass membrane with modified composition using an AC impedance method. The membrane of 218 µm in thickness was sandwiched between two gold electrodes prepared with DC sputtering. The complex impedance diagram measured in the AC frequency range from 1.0 Hz to 100 KHz is presented in Fig. 2. The low frequency intercept (at Z"=0) gives the value of the cell active resistance. Ionic conductivity of the glass was determined to be (1.0-1.2)x10^{-4} S/cm. Accordingly, this glass is one of the best known Li-ion conductors.

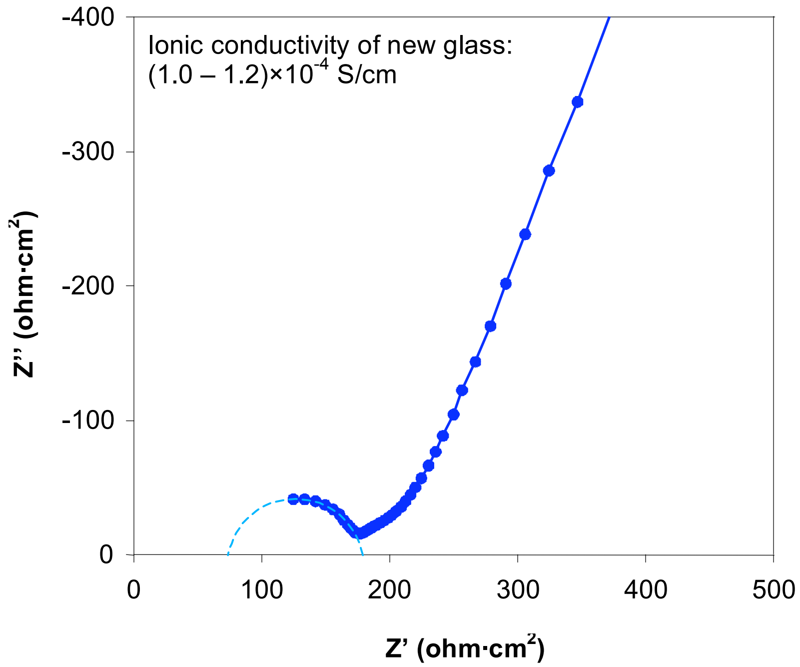

Figure 2. Impedance diagram for 218 µm thick glass membrane sandwiched between two gold electrodes

The potential-time discharge curve obtained for Li protected with this glass in 4 M solution of NH_4Cl is shown on Fig. 3. At a current density of 1.0 mA/cm^2 the Li electrode exhibits a discharge plateau at approximately 2.6-2.7 volts vs. SHE. Discharge capacity delivered so far corresponds to the dissolved Li thickness of 342 µm. The test is in progress.

<u>LiCl based electrolyte, new composition of glass membrane</u>

In this case we used a neutral electrolyte containing 1 M LiCl and a glass membrane with the same composition as in the previous experiment. The LiCl solution does not have any buffer capacity, so the product of cell discharge, LiOH, is formed continuously as the discharge proceeds. As one can see in Fig 4, at a current density of 1.0 mA/cm^2 the Li electrode has a flat voltage-time profile at approximately 2.5-2.7 volts vs. SHE.

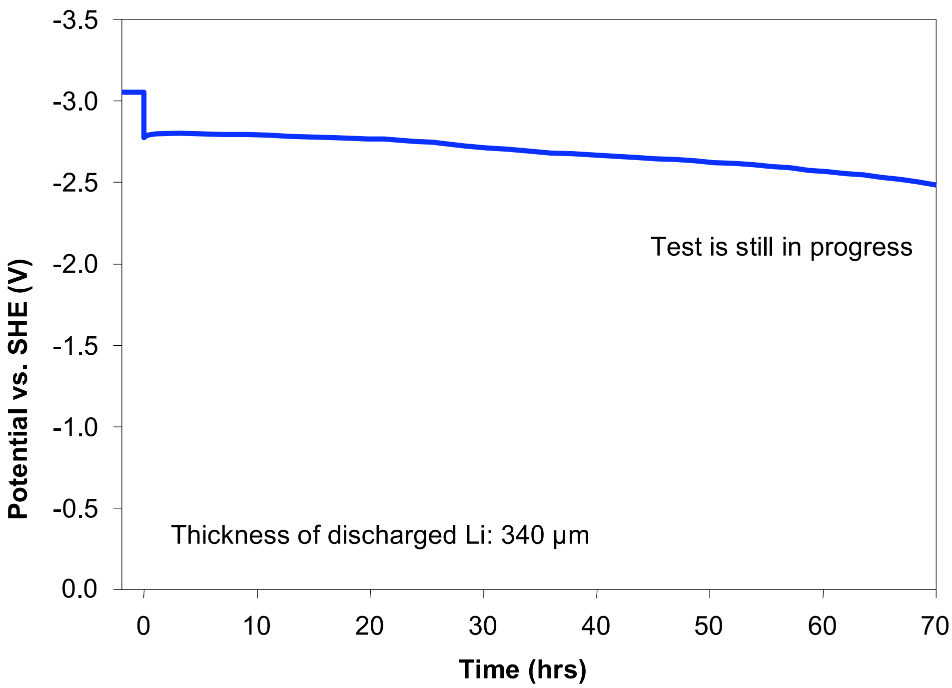

Figure 3. Discharge of thick Li electrode protected with 300 µm glass membrane (new composition) in 4M NH_4Cl aqueous electrolyte at 1.0 mA/cm^2

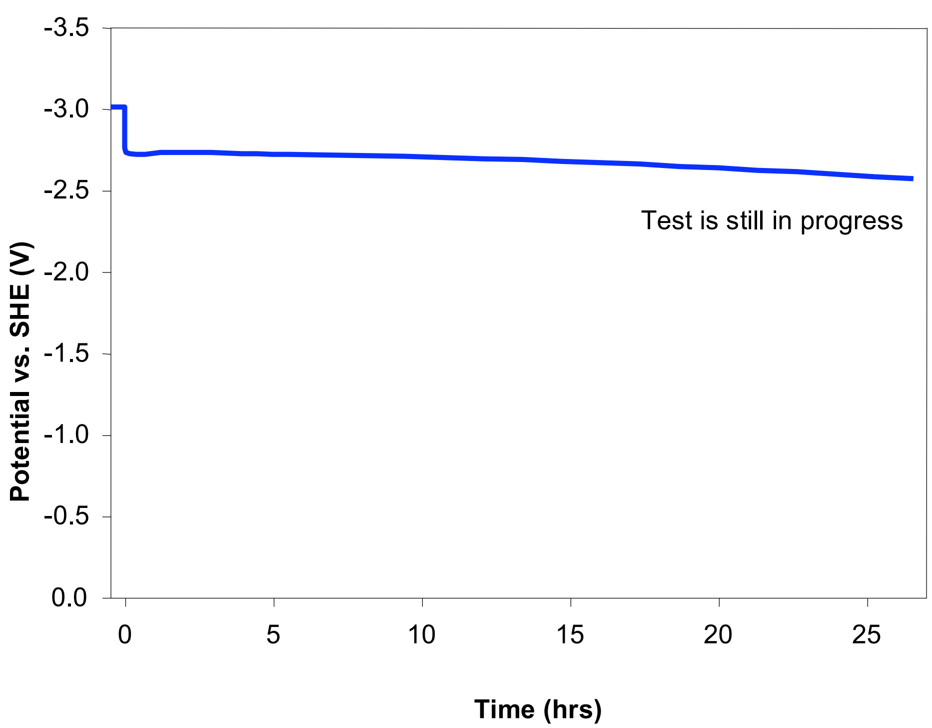

Figure 4. Discharge of thick Li electrode protected with 300 µm glass membrane (new composition) in 1M LiCl aqueous electrolyte at 1.0 mA/cm^2.

Electrochemical experiments on anodic dissolution of thick Li will be continued in various aqueous electrolytes both for standard composition of the protective glass membrane and for glass with modified composition.

2.1 Effect of glass thickness

In this sub-task we study behavior of the protected Li anode under current and determine the anode rate characteristics as a function of the thickness of protective glass membrane. The initial experiments on determination of anodic polarization for the membranes having various thicknesses were described in the May 2004 report. The main aim of this work for the month of June was to find out if the glass with standard composition available from a glass manufacturer in the form of the 50 μm plate can provide a satisfactory polarization at moderate current rates. As expected, the draw-down process will allow us to fabricate the glass sheets with such thickness or even with two-three times lower thickness quite routinely.

In the experiments described below we used Li anodes with a thickness of 3.2 mm. The anode protected fabricated with a 50 μm thick glass membrane was discharged simultaneously with the anode protected having a 300 μm glass membrane. The composition of the interlayer between the Li metal surface and the glass membrane was also different from that used in the experiments described in the May 2004 report. The electrolyte - an aqueous solution of 4 M NH_4Cl - was able to buffer the cathode during cell discharge. The Li/water cells were sequentially discharged at current densities of 2.0, 1.0 and 0.5 mA/cm^2. The testing procedure was designed in such a way that 50 μm of Li was stripped at each step of discharge. In order to maintain the 50 μm discharge capacity at various rates, we used discharge times of 5, 10 and 20 hrs for 2.0, 1.0 and 0.5 mA/cm^2 current densities, respectively. The Li anode protected with a 50 μm thick glass membrane exhibited significantly smaller anodic polarization at all current densities compared to the Li anode protected with a 300 μm glass membrane. Importantly, at 2.0 mA/cm^2 only the anode with the thick glass membrane exhibited significant polarization during discharge. In contrast, the Li anode protected with a 50 μm thick glass exhibits quite acceptable anodic polarization at all current rates used in this study. Anodic polarization seems to be a function of the electrolyte nature and the glass properties, possibly including its composition and surface reactivity. The experimental data demonstrate that improvement in performance of the protected Li anodes can be achieved by further reducing the thickness of the glass membrane.

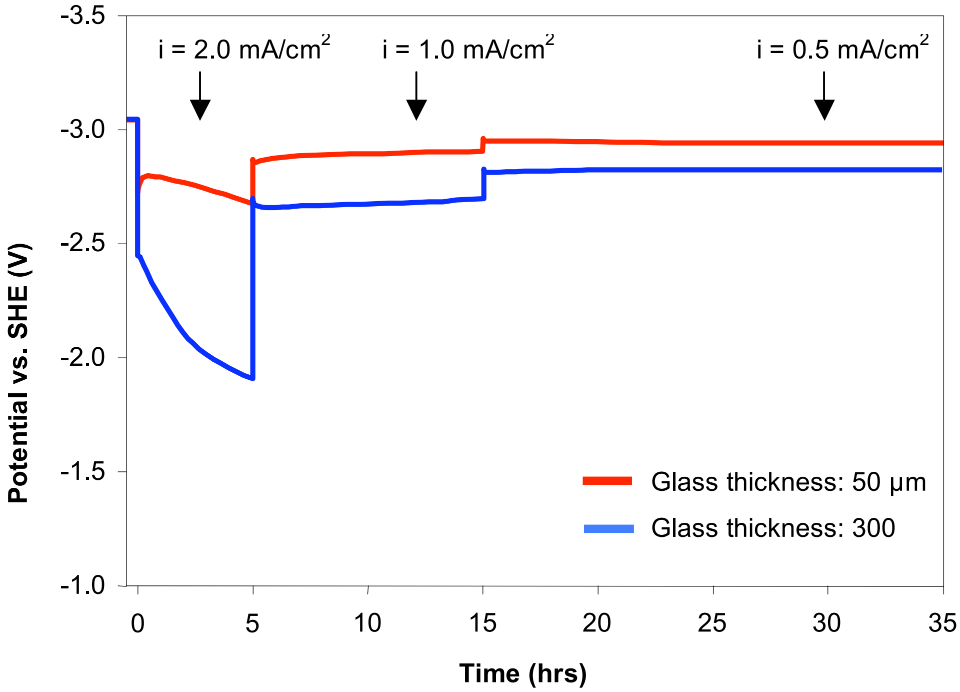

Figure 5. Sequential discharge of lithium electrode with two different thicknesses of glass membrane at 2.0 mA/cm^2, 1.0 mA/cm^2, and 0.5 mA/cm^2 in 4M NH_4Cl aqueous electrolyte

Defense Advanced Research Projects Agency
Defense Sciences Office

Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company July 2004 Report

Technical Highlights

Scheduled tasks: In the forth contract month, key tasks involved tests of anode capacity as a function of Li metal thickness and determination of the Li anode polarization as a function of discharge rate in neutral electrolytes. Also, we continued characterization of the solid electrolyte membranes used for Li protection and started working on performance projections for Li/Air prismatic batteries. All scheduled tasks were completed and the data are described below. PolyPlus achieved discharge of more than 2 mm of Li through the protective membrane in neutral electrolyte. Our experiments show that the voltage drop across the membrane is the main factor contributing to the polarization of the protected anode.

Advanced Li anodes	WBS	Start Date	Finish Date
Half-cell Design	1	4/1/04	4/15/04
Li anode performance	2	4/15/04	9/15/04
Anode capacity as a fcn of Li thickness	2.1	4/15/04	7/30/04
Effect of glass thickness	2.2	5/3/04	6/30/04
Rate characteristics	2.3	6/16/04	8/31/04
Rate as a fcn of temperature	2.4	8/2/04	9/15/04
Aqueous electrolytes for Li/air	3	6/1/04	8/31/04
Acidic electrolytes	3.1	6/1/04	6/30/04
Neutral electrolytes	3.2	7/1/04	7/30/04
Basic electrolytes	3.3	8/2/04	8/31/04
Li/air & Li/water projections	4	9/1/04	9/30/04
Li/air estimates	4.1	9/1/04	9/24/04
Li/water estimates	4.2	9/1/04	9/15/04
BA 5590 projection	4.3	9/30/04	
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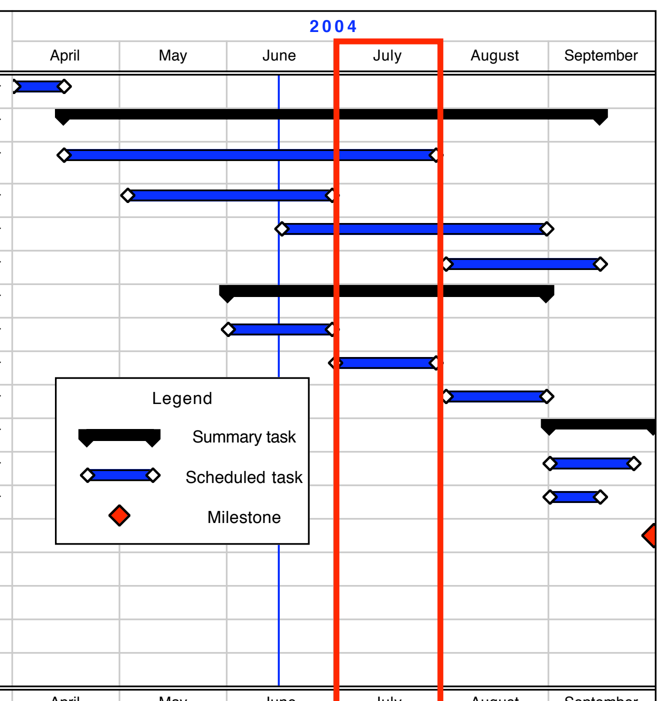


Task 2: Glass Protected Li anode performance

Fabrication of thick Li foils:

Li electrodes with a thickness of 3.0-3.5 mm were fabricated using the method developed at PolyPlus and described in the previous reports. The technique involves extrusion and rolling of the Li foil followed by static pressing of the foil onto the surface of the Ni current collector with a hydraulic press using a die with a polypropylene body.

Aqueous electrolyte:

Li/Water cells used in our experiments on discharge of protected Li were filled with an aqueous electrolyte consisting of 4.0 M of NH_4Cl. Solubility of NH_4Cl in water at 20° C is approximately 4.5 M and increases with temperature. Both discharge products - LiCl and NH_3 - have even higher solubilities. The use of NH_4Cl electrolyte allows us to buffer the cathode and avoid formation of lithium hydroxide, and therefore, prevent electrolyte from carbonization not only during cell initial storage, but also during cell discharge to a significant depth. A Ti screen was used to facilitate electrochemical evolution of hydrogen on the cathode surface.

Results of electrochemical testing:

Capacity as a function of lithium thickness

The potential-time curve for continuous discharge of protected Li anode in aqueous solution of 4 M NH_4Cl is shown on Fig. 1. The cell exhibited a long discharge for over 800 hrs at a closed circuit voltage of approximately 2.8-2.9 V. The value of achieved discharge capacity was very large. More than **2mm of Li** was moved across the Li anode/aqueous electrolyte interface without destruction of the 50 µm thick protective glass-ceramic membrane. The value of Li discharged capacity in this experiment is significantly larger than the Li thickness reported in the June 2004 report. The test is still in progress, so we expect to achieve even larger Li discharge capacity. This result demonstrates excellent mechanical properties of the glass-ceramic membranes and stability of the protected anode under used discharge current.

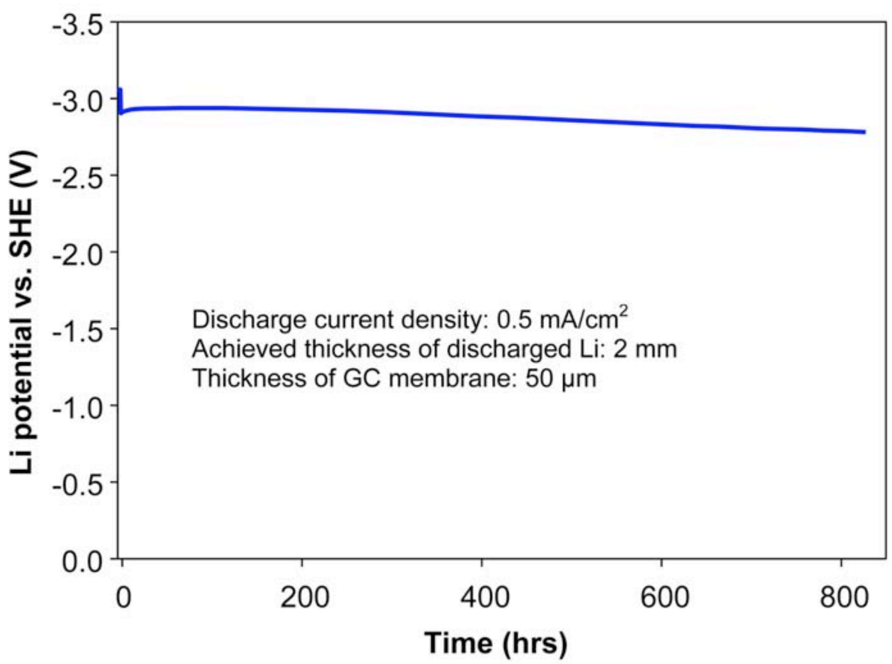


Fig. 1. ***Discharge of 3 mm thick protected Li in 4 M NH_4Cl aqueous electrolyte at 0.5 mA/cm^2***

Characterization of glass-ceramic membrane with new composition: evaluation of electronic current across the membrane in the cell with protected Li

In the following experiments we used a glass membrane with a modified composition. This glass does not contain Ti^{4+} ions and is more stable to reduction than the standard glass used in most of our previous experiments. As we have already mentioned in the June 2004 report, this glass has much better mechanical properties and is easier to produce in the form of a large thin sheet using a draw-down technique. In the previous report we showed AC impedance data obtained in solid-state cells **Au | GC membrane | Au** and demonstrated that this glass is one of the best known Li ion conductors.

Numerous experiments performed at PolyPlus have demonstrated that protected Li has a very low rate of corrosion in aqueous electrolytes. In particular, we have never observed evidence of hydrogen gas evolution on the surface of the protected anode during its storage or discharge in aqueous electrolyte. Still, it is useful to evaluate the actual corrosion rate for protected anode. In Li/Water and Li/Air cells with GC protected anode there is complete separation of Li from the liquid aqueous electrolyte. Therefore, the Li corrosion rate is determined only by the electronic transport across the GC membrane. Similar to other solid electrolytes, in addition to ionic conductivity, GC electrolytes have a specific value of conductivity associated with electronic minority charge carriers (an important difference between solid and liquid electrolytes). In our case we are interested in the electronic leakage currents across the GC, which is in contact with Li metal.

Determination of partial electronic conductivity of predominantly ionic conductors is based on the measurements of steady state currents in an asymmetric polarization cell of the type shown on Fig. 2. In this solid-state cell the solid electrolyte is sandwiched between a reversible electrode, in our case protected Li, and ion blocking inert electrode, in our case vacuum deposited Au film. In figures 3a and 3b we show chronoamperometric curves obtained for such a cell after applying a potential of 3.25 V. Forty-five hours after the potential step was applied, the current reached the value of $5x10^{-11}$ A/cm^2. This result shows that the electronic current across the GC membrane is less than 50 pA/cm^2. Accordingly, the corrosion rate of the GC protected Li is effectively zero.

Fig. 2. Schematic view of asymmetric polarization solid-state cell used for determination of electronic current across glass-ceramic membrane

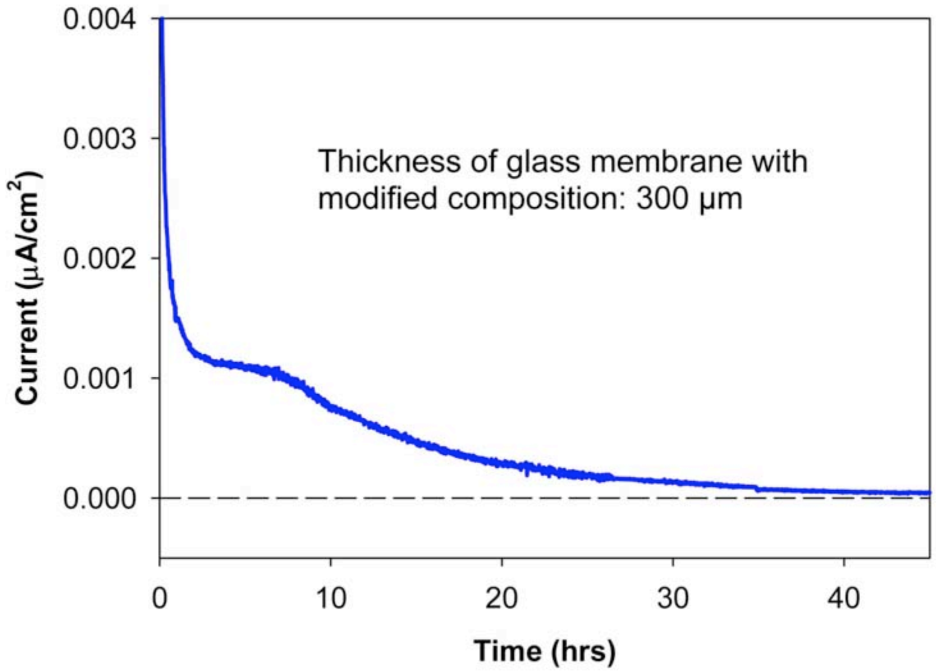


Fig. 3a. Evaluation of electronic current in cell with GC membrane and protected Li anode: chronoamperometry after applying a potential of 3.25 V

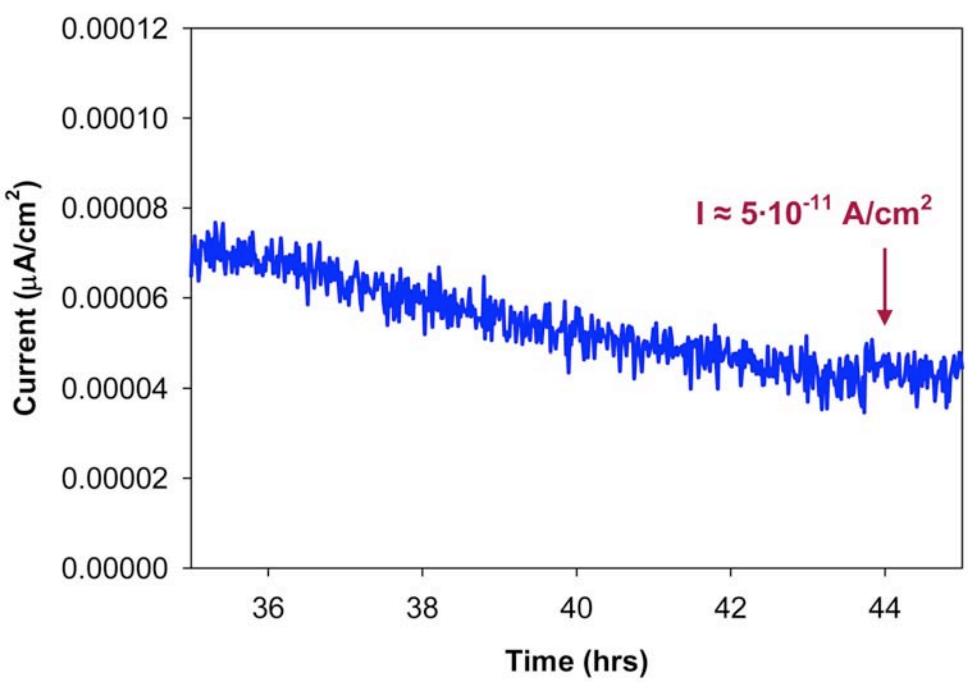


Fig. 3b. Evaluation of electronic current in cell with GC membrane and protected Li anode: final portion of chronoamperometric curve after applying a potential of 3.25 V

Rate characteristics

In this sub-task we study the anode rate characteristics in neutral aqueous electrolyte. The experiments on determination of anodic polarization for the membranes having various thicknesses were described in the May 2004 report. The main focus of the work in the month of July was to determine polarization at various discharge rates for the anode protected with the glass having modified composition. This glass is currently available from a glass manufacturer in the form of a 150 µm membrane. As we have mentioned in the previous report, we expect that the draw-down process will allow us to fabricate glass sheets with three to six times lower thicknesses.

In the experiments described below we used Li anodes with a thickness of 3.2 mm. The anode protected with a 150 µm thick glass membrane was sequentially discharged at the current densities of 0.5, 1.0, 2.0, 4.0, 6.0, and 8.0 mA/cm^2. In figures 4a and 4b we show the discharge potential and polarization of the Li anode vs. discharge current density. These values were determined from experimental chronopotentiogramms one minute after the current was applied. The electrolyte - an aqueous solution of 4 M NH_4Cl - was able to buffer the cathode during cell discharge. As expected, the anode polarization rises with increase in the rate of discharge. In general, anodic polarization is a function of the nature of electrolyte and properties of the glass-ceramic, possibly including its composition and surface reactivity. Under conditions of our experiments, the voltage drop across the membrane appears to be the main contributor to the polarization of the protected anode. The experimental data implies that improvement in performance of the protected Li anodes can be achieved by further reduction of the thickness of the glass membrane.

Electrochemical experiments on the anodic dissolution of protected Li in various aqueous electrolytes will be continued in the month of August both for the standard composition of the protective glass-ceramic membrane and for glass-ceramic membranes with modified chemical composition.

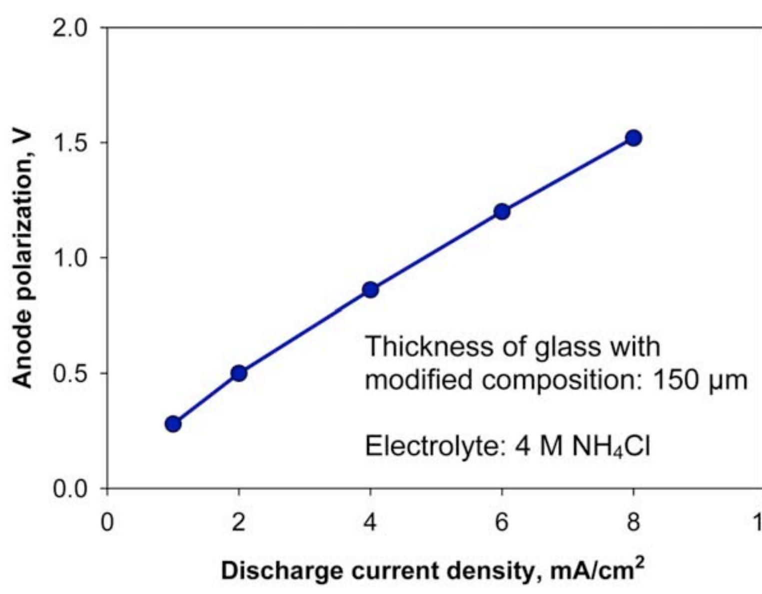


Fig. 4a. Li anode potential as a function of discharge current density

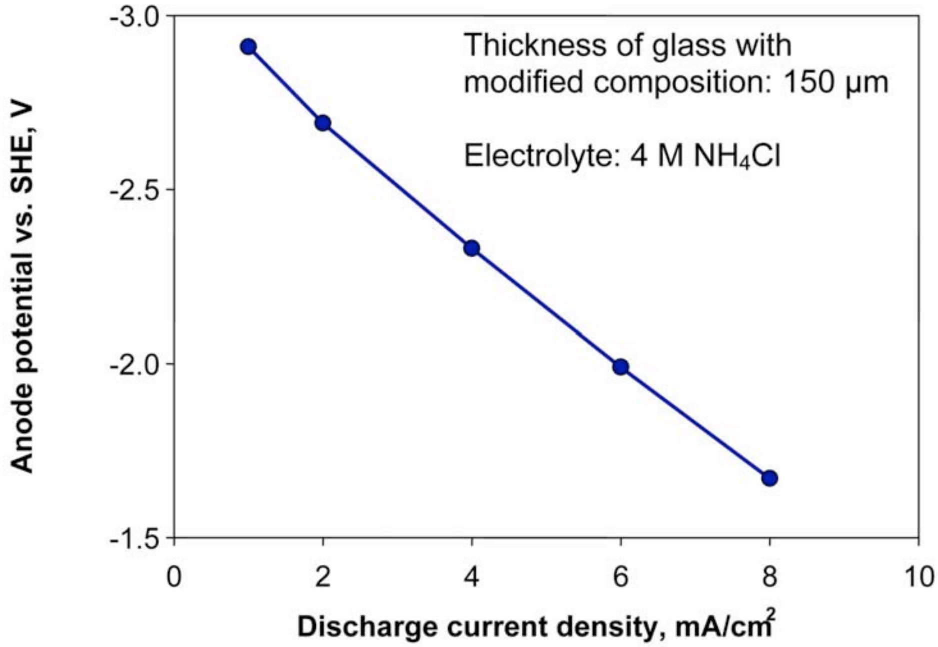


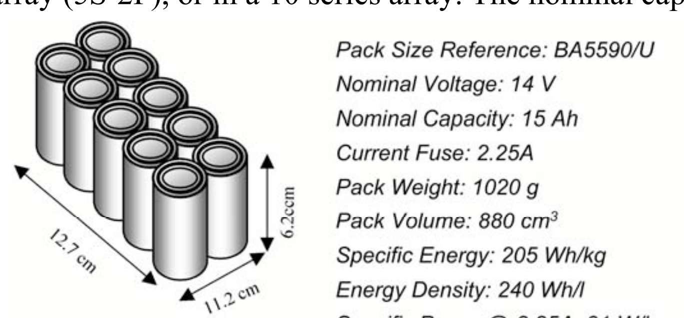
Fig. 4b. Polarization of protected Li anode as a function of discharge current density

Preliminary Cell Design Projections

Preliminary Li-Air battery pack projections were done is such a way that the shape of the individual cells and battery packs match those of the BA 5590/U pack and its component Li/SO_2 R20-D size cells. Furthermore, the Li-Air cell projections and its pack configurations are designed to meet the following performance criteria: working voltage of 15V and 30W of average power for a 24-hour period (720 Wh delivered); and, with the desired battery pack weighing less than 2lbs, the corresponding specific energy requirement is 800Wh/kg.

BA-5590 Pack

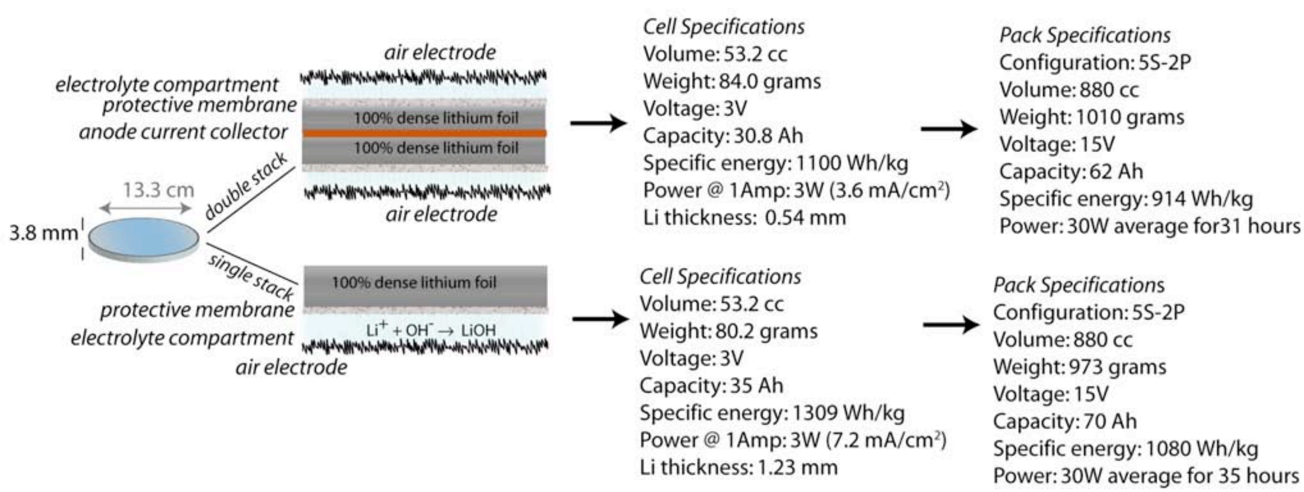
The BA5590 battery pack comprises ten Li-SO_2 R20-D size cells. The cells are either configured in a 5 series/ 2 parallel array (5S-2P), or in a 10 series array. The nominal capacity of the individual R20-D cells is 7.5Ah (based on a 240mA drain) with a nominal voltage of 2.8V. The volume of the R20-D cylindrical cells is 53.2 cc, and it has a specific energy of 250 Wh/kg. The BA-5590 pack (5S-2P) is nominally rated at 14V and has a maximum drain rate of about 2A[1]. The capacity is rated at 15Ah, and the specific energy of the pack is 200 Wh/kg. At a current drain of 2.2 Amps the BA5590 pack should deliver 30W for about a 7 hours of run-time.

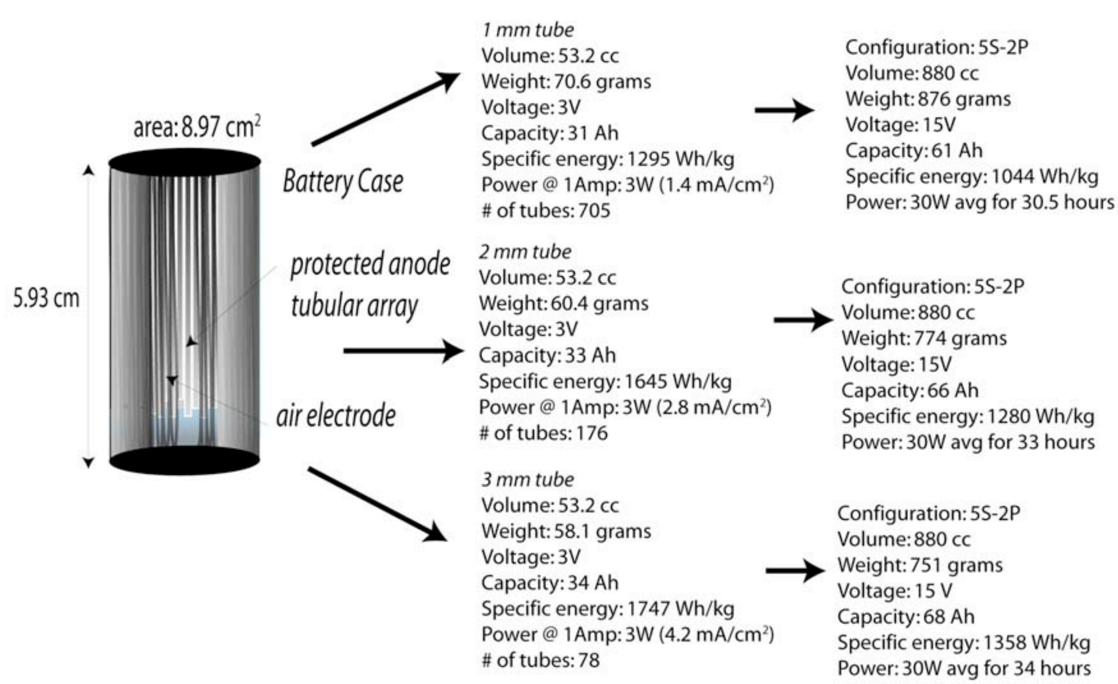


[1] SAFT website

Single Cell Designs (Flat Prismatic and Cylindrical with a Tubular Array)

Diagrams of Li-Air cells, including both the casing and the internal construction for the flat plate prismatic and the cylindrical tubular array are shown below. For the purpose of these projections the cylindrical cells were designed to match both the size and shape of the R20-D Li/SO2 cell used in the BA5590/U, while the prismatic cell was designed to only match the volume of the R20-D. In the case of the flat prismatic cells, both a single stack and double stack design are used in the performance projections. The advantage of a double stack is to increase the anode area, albeit at a slight sacrifice in energy.





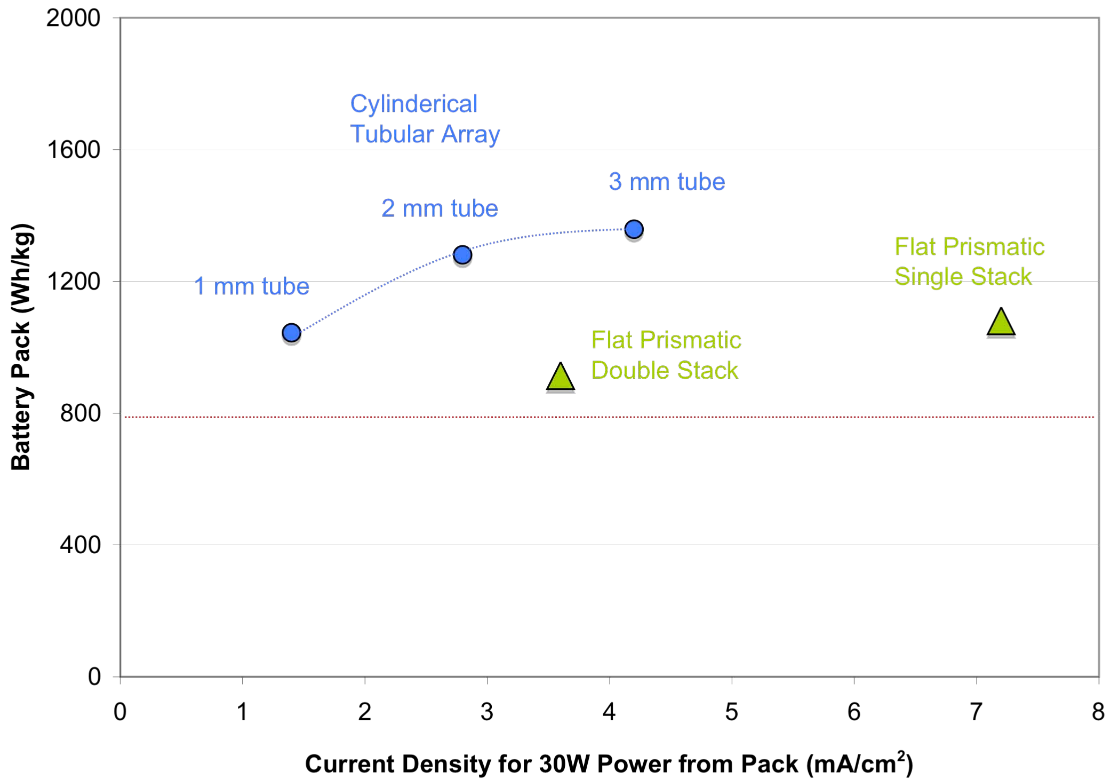


Figure 5. ***Projections for 900 Wh Li/Air battery packs; flat & tubular membranes; specific energy for various configurations and the corresponding current density needed to sustain 30 W drain rate***

Defense Advanced Research Projects Agency
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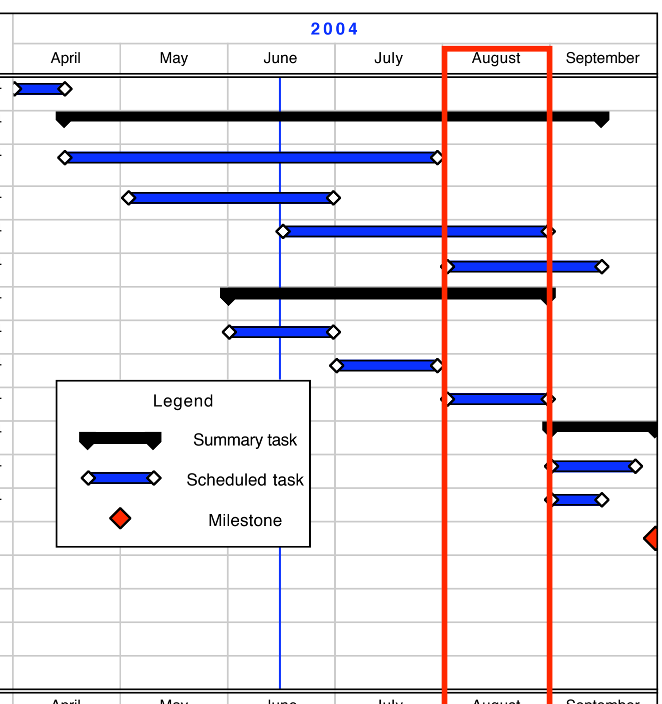
Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company August 2004 Report

Technical Highlights

Scheduled tasks: In the fifth contract month, key tasks involved tests of anode capacity as a function of Li metal thickness and measurements of rate characteristics in neutral electrolytes at various temperatures. Also, we determined the Li anode polarization in basic electrolytes as a function of discharge rate after various periods of cell storage and worked on performance projections for Li/Air prismatic batteries using the value of experimentally achieved Li discharge capacity. All scheduled tasks were completed and the data are described below. PolyPlus demonstrate discharge of 3.35 mm of Li through the 50 µm thick protective membrane in neutral electrolyte. This achievement makes possible the development of Li/Air batteries with exceptionally high specific energy. Our experiments also show that the voltage drop across the membrane is the main factor contributing to the polarization of the protected anode at various temperatures and that the glass protected anode has quite an acceptable anodic polarization at moderate current rates in a wide temperature range.

Advanced Li anodes	WBS	Start Date	Finish Date
Half-cell Design	1	4/1/04	4/15/04
Li anode performance	2	4/15/04	9/15/04
Anode capacity as a fcn of Li thickness	2.1	4/15/04	7/30/04
Effect of glass thickness	2.2	5/3/04	6/30/04
Rate characteristics	2.3	6/16/04	8/31/04
Rate as a fcn of temperature	2.4	8/2/04	9/15/04
Aqueous electrolytes for Li/air	3	6/1/04	8/31/04
Acidic electrolytes	3.1	6/1/04	6/30/04
Neutral electrolytes	3.2	7/1/04	7/30/04
Basic electrolytes	3.3	8/2/04	8/31/04
Li/air & Li/water projections	4	9/1/04	9/30/04
Li/air estimates	4.1	9/1/04	9/24/04
Li/water estimates	4.2	9/1/04	9/15/04
BA 5590 projection	4.3	9/30/04	
	5		



Task 2: Glass Protected Li anode performance

Fabrication of thick Li foils:

Li electrodes with a thickness of 3.3-3.5 mm were fabricated using the method developed at PolyPlus and described in the previous reports. The technique involves extrusion and rolling of the Li foil followed by static pressing of the foil onto the surface of the Ni gauze current collector with a hydraulic press. A die with a polypropylene body was used for the pressing operation to avoid chemical reaction with the lithium foil.

Aqueous electrolyte:

Li/Water cells used in our experiments for long discharge of protected Li and for determination of rate characteristics at various temperatures were filled with aqueous electrolytes based on NH_4Cl. The use of NH_4Cl electrolyte allowed us to buffer the cathode during cell storage and discharge. For determination of the Li anode polarization as a function of discharge rate after various periods of storage we used a basic electrolyte consisting of 1.0 M LiOH. A Ti screen was used to facilitate electrochemical evolution of hydrogen on the cathode surface.

Results of electrochemical testing

Capacity as a function of lithium thickness

The potential-time curve for continuous discharge of protected Li anode in aqueous solution of 4 M NH_4Cl is shown on Fig. 1. The cell exhibited a very long discharge for almost 1400 hrs at a closed circuit voltage of approximately 2.7-2.9 V. The value of achieved discharge capacity was very large. More than **3.35 mm of Li** was moved across the Li anode/aqueous electrolyte interface without destruction of the 50 μm thick protective glass-ceramic membrane. The thickness of the Li foil used in this experiment was in the range of 3.35-3.40 mm. Postmortem analyses of the discharged Li anode confirmed that the full amount of Li was stripped from the Ni current collector at the completion of the cell discharge. It shows that coulombic efficiency for discharge of the glass protected Li anode is close to 100%. The value of Li discharged capacity achieved in this experiment is very large, but we expect to further increase the amount of Li passed across the same membrane by using this membrane in the cell with a new 3 mm thick Li foil. Such an experiment has been already started.

Battery projections based on achieved Li discharge capacity values

PolyPlus used the Li discharge capacity shown in figure 1 to project performance of Li/Air prismatic batteries. In Fig. 2 we show specific energy projections for Li-Air batteries with varying thickness of protected Li and the value of cell gravimetric specific energy for a glass protected anode with Li thickness of 3.3 mm. Figure 2 also illustrates the cell configuration and parameters used for the calculations. The cell dimensions correspond to the area of a business card (45 cm^2) and about 6 mm thickness; this yields a huge 90 Wh projected capacity. As one can see from Fig. 2, the experimentally achieved discharge capacity of glass-protected anode allows for construction of Li/Air batteries with exceptionally high volumetric and gravimetric energy density.

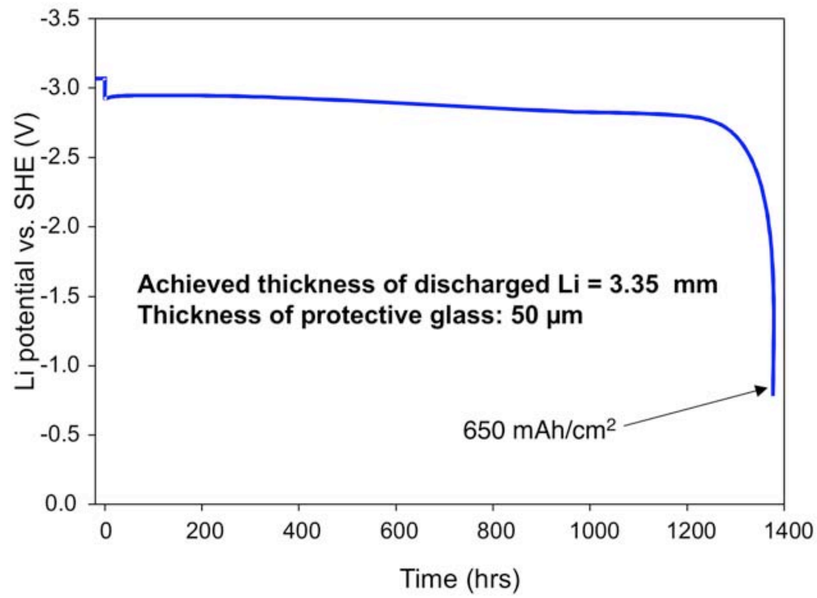


Fig. 1. Discharge of thick protected Li in 4 M NH_4Cl aqueous electrolyte at 0.5 mA/cm^2.

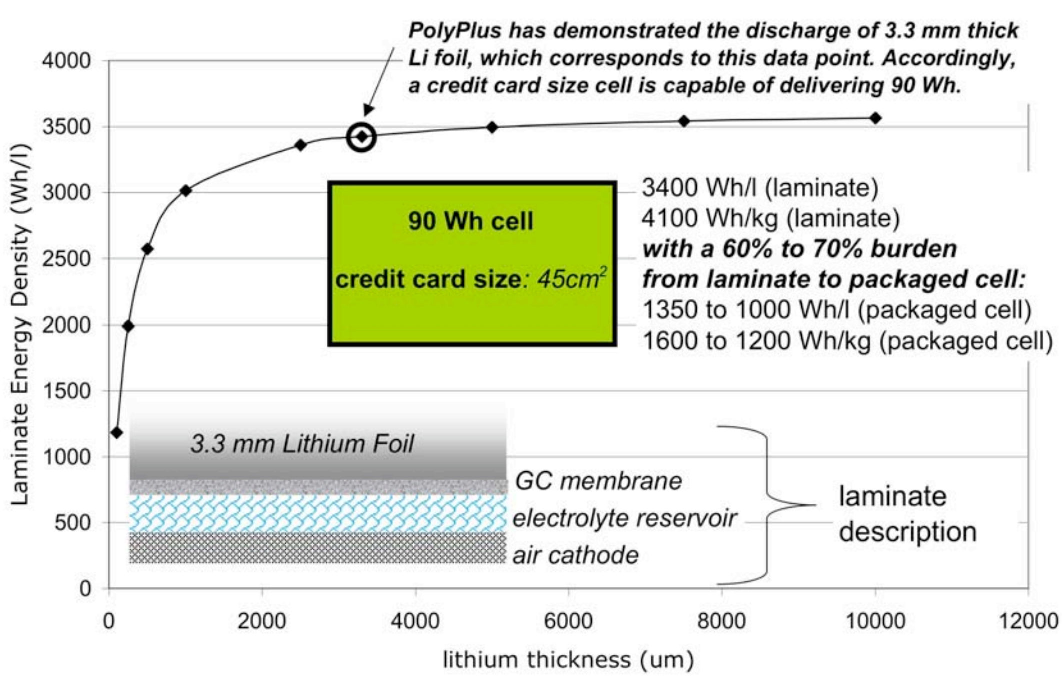


Fig.2 Specific energy projections for Li/Air battery

Li anode performance in basic electrolyte

In these experiments we used the Li anodes with a thickness of 3.3 mm. A Li anode protected with a 300 μm thick glass membrane was sequentially discharged at the current densities of 0.5, 1.0, 2.0, and 4.0 mA/cm^2 after various periods of cell storage under open circuit conditions. The electrolyte solution contained 1 M LiOH. This testing procedure was designed in such a way that the duration of discharge at each rate was 20 minutes and accordingly, discharge capacity at 4.0 mA/cm^2 was eight times greater than at 0.5 mA/cm^2.

As one would expect, the anode polarization rises with increase in the rate of discharge (Fig. 3). In addition, the length of cell storage slightly affects the value of anode polarization. This effect is more pronounced at higher discharge rates. In general, anodic polarization is a function of the electrolyte nature and the glass properties, in particular its composition and surface reactivity. It is not surprising that strongly basic electrolyte affects the surface of glass-ceramic membrane. PolyPlus is currently performing experiments to determine long-term stability of glass membranes in a variety of aqueous electrolytes. It has already been found that the present composition of glass is stable in neutral electrolytes, in particular, electrolytes based on NH_4Cl aqueous solutions. Therefore, such electrolytes can be used to avoid contact of the glass with basic LiOH solutions during cell storage and the main portion of cell discharge. Also, it is possible to modify the glass composition in order to improve its stability in basic solutions. PolyPlus has already started this work.

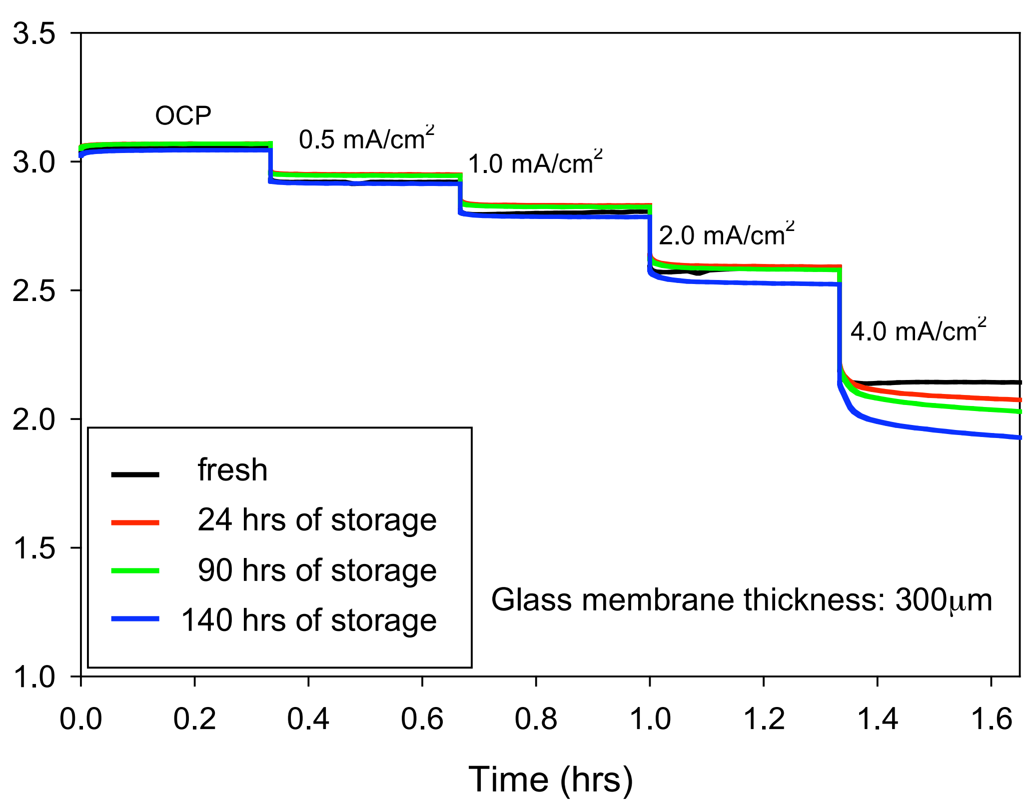


Fig.3 Sequential discharge of protected Li electrode in 1M LiOH electrolyte at 0.5, 1.0, 2.0 and 4.0 mA/cm^2 after various periods of storage.

Rate characteristics at various temperatures

In this sub-task we study the anode rate characteristics in neutral aqueous electrolyte as a function of temperature. The aim of this work for the month of August was to determine anode polarization at various discharge rates in the temperature range from 5 to 60 ºC for the anode protected with a 150 um thick glass membrane. As we have mentioned in the previous reports, we expect that the draw-down process will allow us to fabricate glass sheets with three to five times lower thicknesses.

In the experiments described below we used Li anodes with a thickness of 3.4 mm. The anode protected with a 150 µm thick glass membrane was sequentially discharged at the current densities of 0.5, 1.0, 2.0, and 4.0 mA/cm^2 at 60, 40, 25, 15 and 5 ºC. In figures 4a and 4b we show the discharge potential and polarization of the Li anode at various temperatures plotted vs. discharge current density. These values were determined from experimental chronopotentiogramms one minute after the current was applied. The electrolyte - an aqueous solution of 1 M NH_4Cl - was able to buffer the cathode during cell discharge. As one would expect, the anode polarization rises with increase in the discharge rate and with decrease in temperature. As it has been reported earlier, under conditions of our experiments the voltage drop across the membrane is the main contributor to the polarization of the protected anode. Reducing the glass membrane conductivity with decrease in temperature leads to the increase in anode polarization. The experimental data imply that improvement in performance of the protected Li anodes in the low temperature range can be achieved by further reducing the thickness of the glass membrane. The experiments on determination of anodic polarization as a function of temperature for the anodes having membranes with various thicknesses will be continued in the month of September.

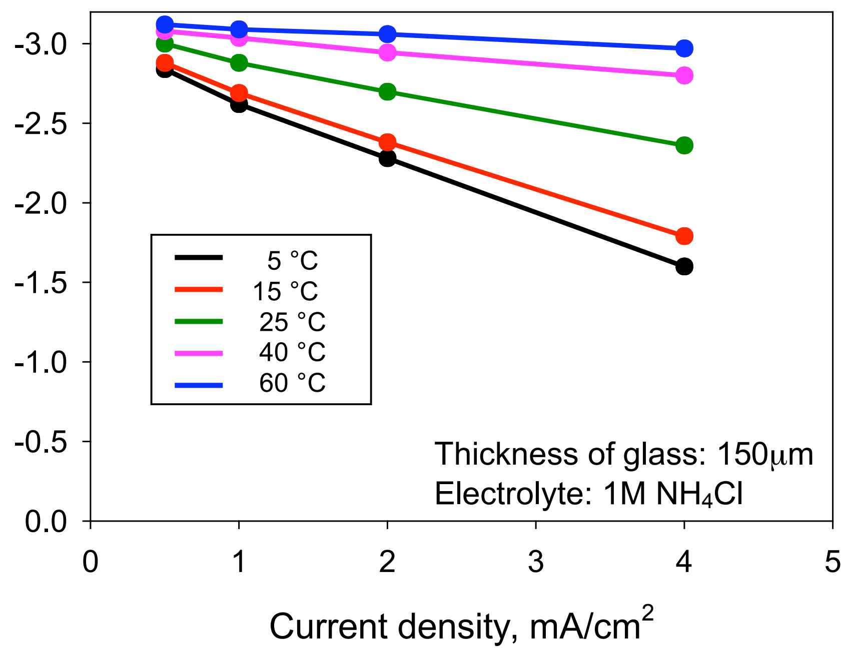


Fig. 4a. Protected Li anode potential as a function of discharge current density at various temperatures.

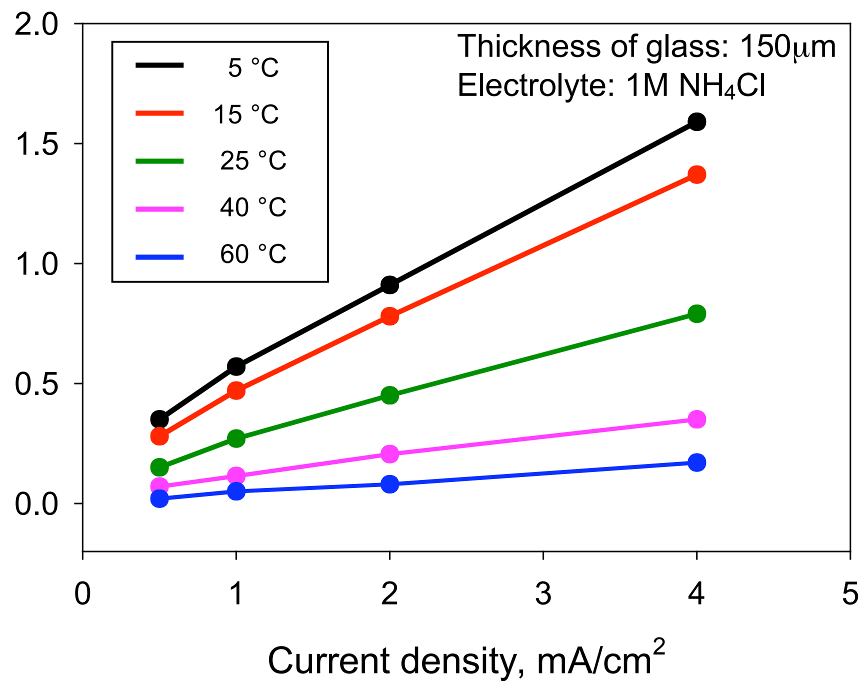


Fig. 4b. Polarization of protected Li anode as a function of discharge current density at various temperatures.

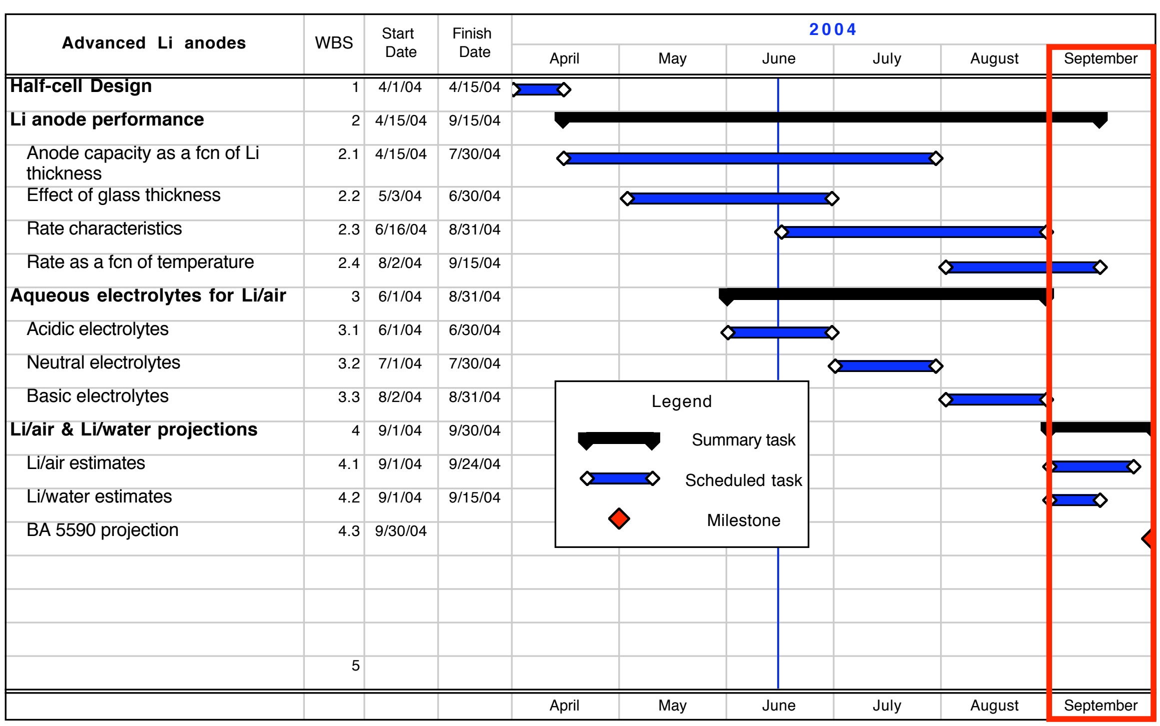
Defense Advanced Research Projects Agency
Defense Sciences Office

Advanced Lithium Anodes for Li/Air & Li/Water Batteries

PolyPlus Battery Company September 2004 Report

Technical Highlights

Scheduled tasks: In the sixth contract month, key tasks involved measurements of rate characteristics at low temperatures and performance projections for Li/Air and Li/Water batteries. Also, we tested Li/air cells filled with neutral electrolyte. All scheduled tasks were completed and the data are described below. Our experiments show that the glass protected anode has quite an acceptable performance at low and moderate current rates even at a temperature as low as -5 ºC. Performance projections demonstrate possibility of design of Li/Air and Li/Water batteries with exceptionally high volumetric and gravimetric energy density.



Task 2: Glass Protected Li anode performance

Fabrication of Li foils

Li electrodes with a thickness of 3.3-3.4 mm were fabricated using the technique of extrusion and rolling of the Li foil followed by static pressing of the foil onto the surface of the Ni gauze current collector with a hydraulic press. This method was described in more detail in our previous reports. Li electrodes with a thickness of 100-125 μm were fabricated by pressing of the 125 μm commercial foil onto the Ni foil current collector. A die used for the pressing operation had a polypropylene body to avoid chemical reaction with the lithium foil.

Aqueous electrolyte

Li/Water cells used for determination of rate characteristics at various temperatures were filled with aqueous electrolytes based on NH_4Cl. Similar electrolyte was used in Li/Air cells. The use of NH_4Cl electrolyte allowed us to buffer the cathode during cell storage and discharge. A Ti screen was used to facilitate electrochemical evolution of hydrogen on the cathode surface in Li/Water cells. A standard air cathode from Rayovac developed for Zn/Air batteries with KOH based electrolyte was used in our Li/Air cells.

Rate characteristics of protected Li anode at low temperatures

In this sub-task we study the anode rate characteristics in neutral aqueous electrolyte as a function of temperature. The aim of this work for the month of September was to determine anode polarization at various discharge rates in the temperature range from -5 to 25 ºC. The anode was protected with a 175 um thick glass-ceramic membrane. It is expected that using the draw-down process we will be able to fabricate glass-ceramic sheets with three to five times lower thicknesses.

In the experiments described below we used Li anodes with a thickness of 3.5 mm. The protected Li anode was sequentially discharged at the current densities of 0.25, 0.5, 1.0, 2.0, and, in some cases, at 3.0 mA/cm^2 at +25, +10, 0, and -5 ºC. In figures 1a and 1b we show the discharge potential and polarization of the Li anode at various temperatures plotted as a function of discharge current density. These values were determined from experimental potential-time or polarization-time curves one minute after the current was applied. The electrolyte, an aqueous solution of 1 M NH_4Cl, was able to buffer the cathode during cell discharge. As one can see in figures 1a and 1b, at a constant current the anode polarization decreases with increase in temperature. The voltage drop across the membrane is the main contributor to the polarization of the protected anode. Decrease in the glass membrane conductivity at low temperatures leads to the increase in anode polarization. The data show that the anode protected with a relatively thick glass of 175 μm has quite an acceptable performance at discharge current densities below 1.0 mA/cm^2 even at a temperature as low as -5 ºC The experimental data imply that further improvement in rate performance of the protected Li anodes at low temperatures can be achieved by reducing the thickness of the protective glass-ceramic membrane.

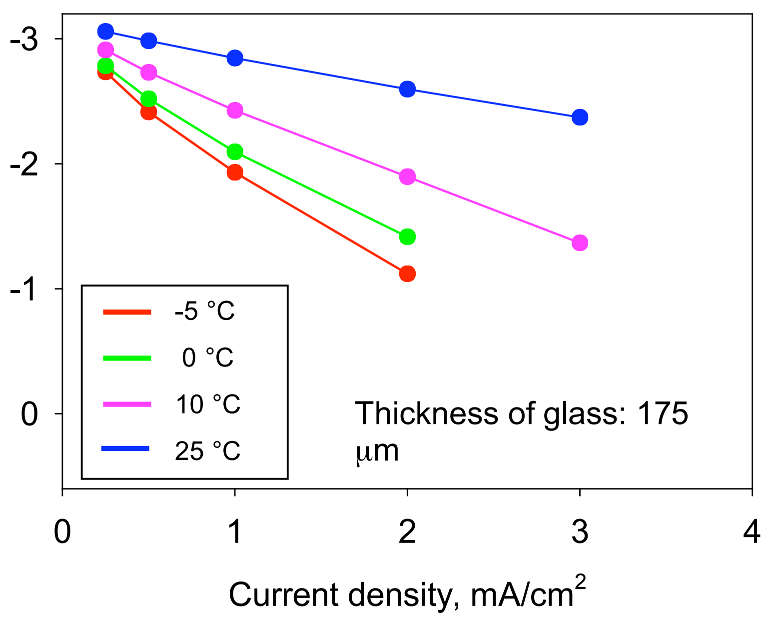


Fig.1a. Protected Li anode potential as a function of discharge current density at various temperatures.

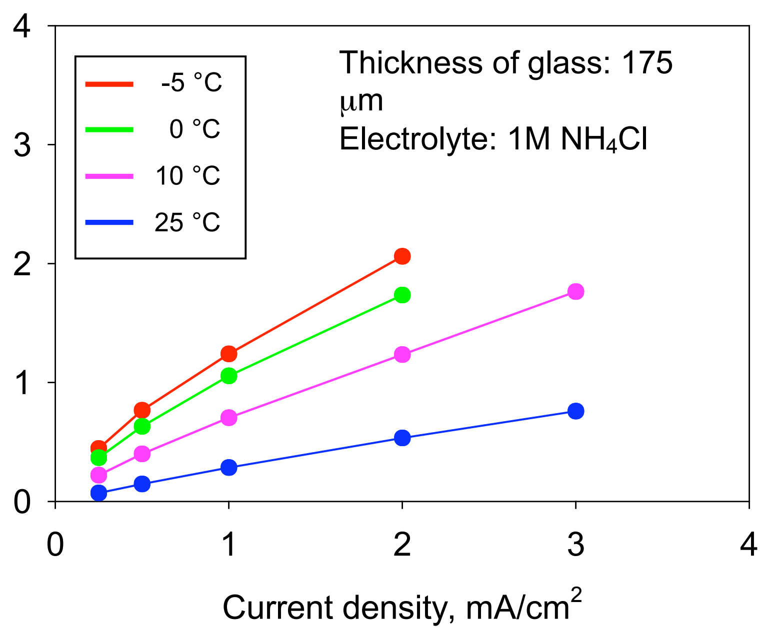


Fig. 1b. Polarization of protected Li anode as a function of discharge current density at various temperatures

Electrochemical testing of protected Li electrode in Li/Air cells with neutral electrolyte

As we have already mentioned in previous reports, aqueous electrolytes based on ammonium chloride are able to buffer the air electrode during cell storage and discharge. Also, glass-ceramic membranes are quite stable in these electrolyte systems. As a continuation of work on characterization of protected Li electrode PolyPlus initiated testing of Li/Air cells with NH_4Cl based electrolytes and standard air cathodes developed for Zn/Air batteries. The thickness of the protective glass was 150 µm, and the thickness of the Li foil on a Cu substrate was 125 µm. The Li/air cell was discharged for more than 34 hrs at a current density of 0.5 mA/cm^2 (Fig. 2). The entire 125 um of lithium was discharged across the protective glass membrane without its destruction. Postmortem analyses of the discharged Li anode confirmed that the full amount of Li was stripped from the Ni current collector at the completion of the cell discharge.

Postmortem analyses of the discharged air electrodes showed that the Ni screen current collector badly corroded during cell discharge and mostly lost connection with the cathode active mass. This is not unexpected because Ni metal is not stable in the acidic and neutral solutions used in these studies. An additional complication of using air electrodes developed for Zn/Air batteries in the Li/Ar cells with NH_4Cl electrolyte was found to be their poor wetting ability towards neutral electrolytes. The experimental data show that existing air electrodes need to be re-designed for use in Li/air batteries with acidic and neutral aqueous electrolytes.

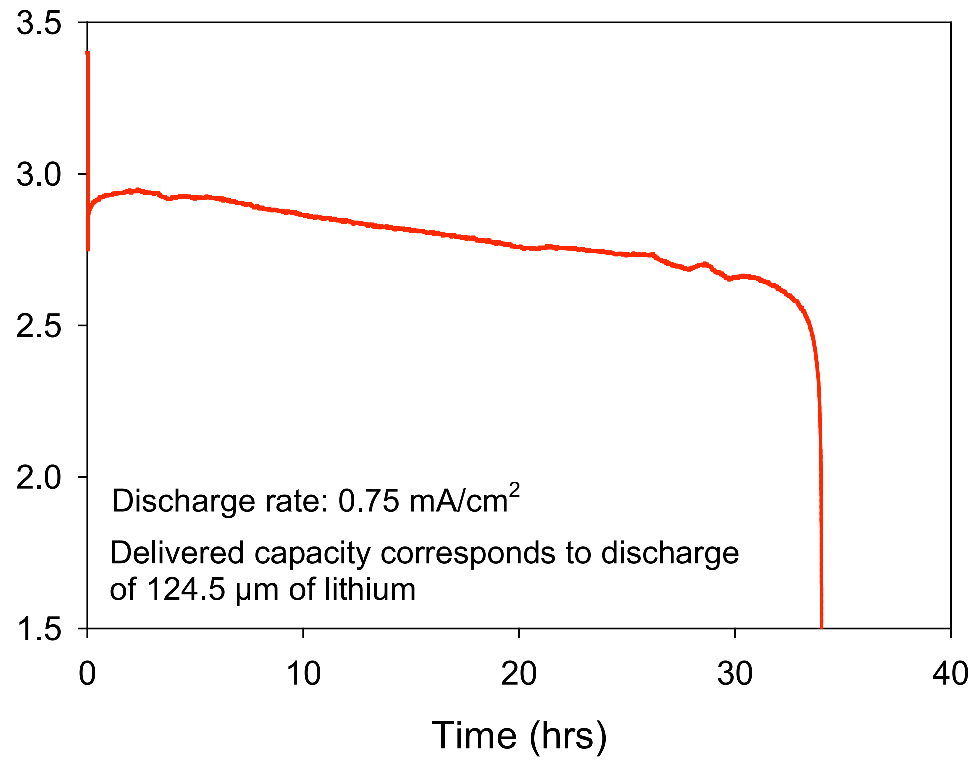


Fig.2 Discharge curve for Li/Air cell with 4 M NH_4Cl electrolyte and 125 µm thick Li

Task 4 Li/Air & Li/Water Projections based on Protected Anode Performance.

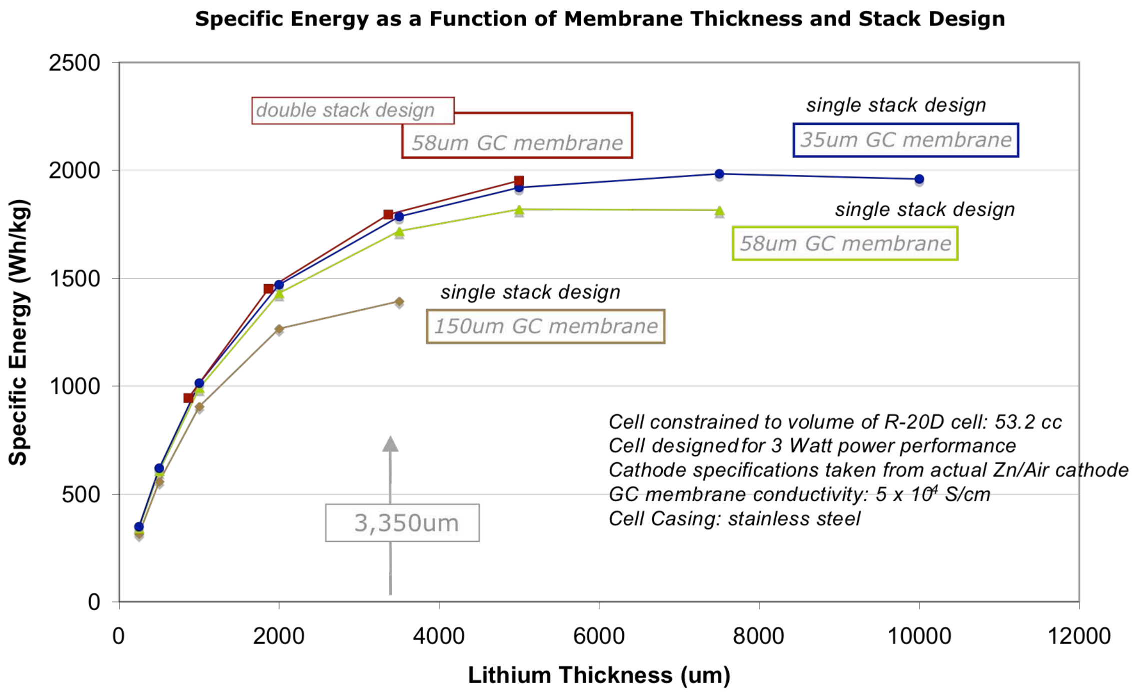


Figure 3. Specific Energy as a function of lithium metal electrode thickness and cell design; planar design used for calculations with single-sided and double-sided discharge of Li foil; specific energy indicated for case where PolyPlus discharged 3.35 millimeters of Li

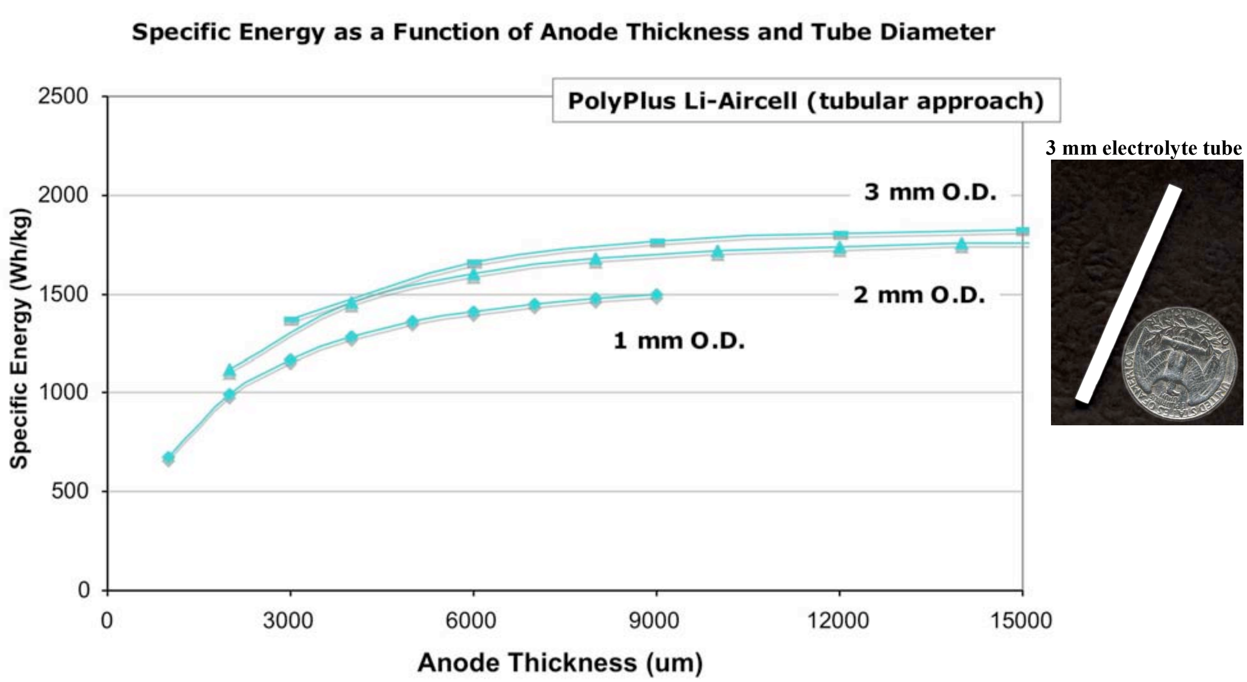
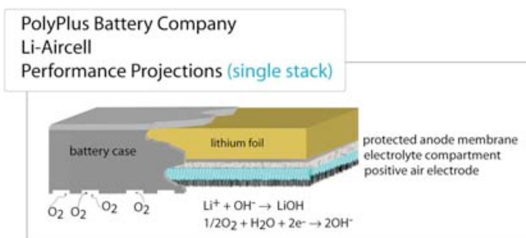


Figure 4. Specific energy projections for Li/Air cells using tubular protected anodes; specific energy as a function of tube diameter & anode thickness; inset at right shows 1st production run of tubular solid electrolyte (3 mm OD, 300 µm wall).

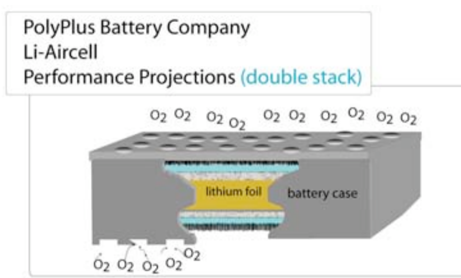


CELL SPECIFICATIONS

Volume: 53.2 cc
Weight: 66 gr
Capacity: 41 Ah
Specific Energy: 1730 Wh/kg
Power: 3 Watts
Li thickness: 3500 um

PACK SPECIFICATIONS

Configuration: 5S-2P
Volume: 880 cc
Weight: 830 gr / 1.8 lbs
Voltage: 13.9 V
Specific Energy: 1370 Wh/kg
Power: 30 W for 38 hours

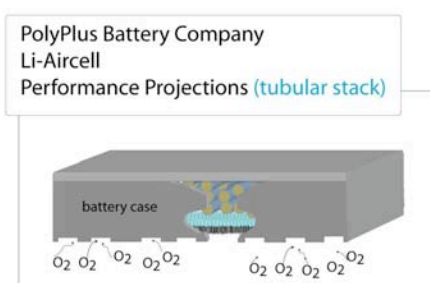


CELL SPECIFICATIONS

Volume: 53.2 cc
Weight: 63 gr
Capacity: 39 Ah
Specific Energy: 1790 Wh/kg
Power: 3 Watts
Li thickness: 3365um

PACK SPECIFICATIONS

Configuration: 5S-2P
Volume: 880 cc
Weight: 800 gr / 1.8 lbs
Voltage: 14.5 V
Specific Energy: 1410 Wh/kg
Power: 30W for 38 hours



CELL SPECIFICATIONS

Volume: 53.2 cc
Weight: 69 gr
Capacity: 35 Ah
Specific Energy: 1500 Wh/kg
Power: 3 Watts
tube diameter: 1mm

PACK SPECIFICATIONS

Configuration: 5S-2P
Volume: 880 cc
Weight: 860 gr / 1.9 lbs
Voltage: 15 V
Specific Energy: 1220 Wh/kg
Power: 30 W for 35hours

Figure 5. Projections of Li/Air chemistry into BA 5590 packaging; topmost battery uses single-sided cell, middle battery built with double-sided cells, and bottom battery is based on tubular protected Li.

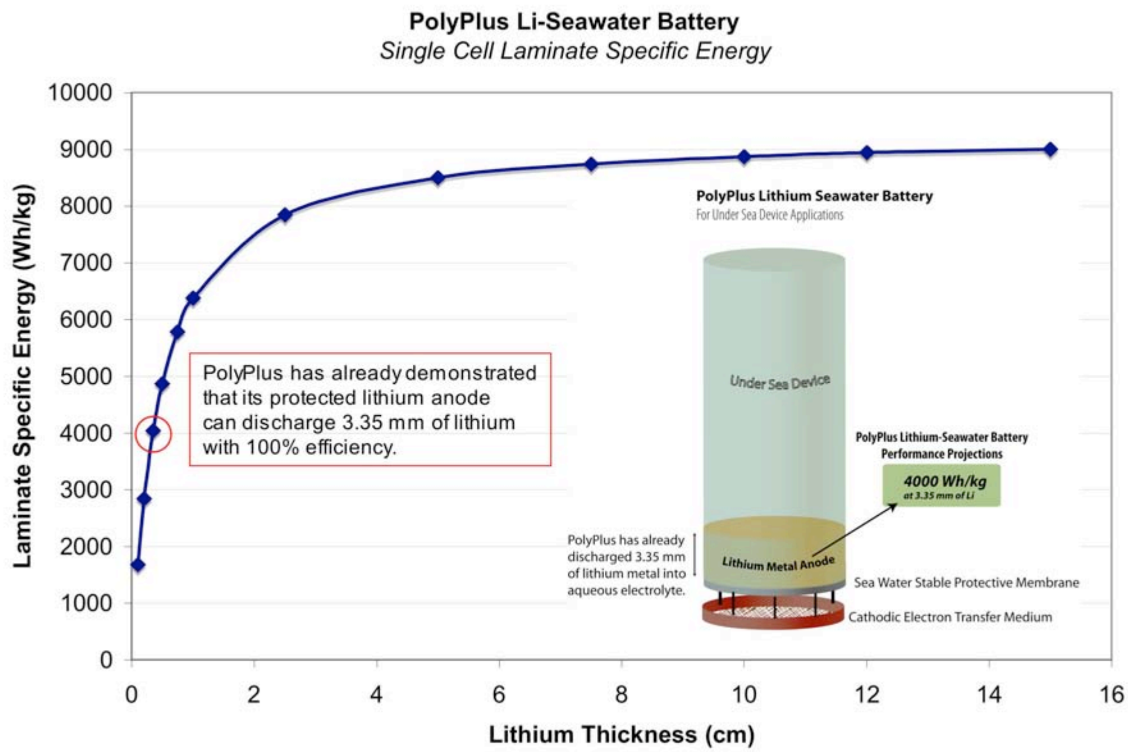


Figure 6. Projections for protected lithium electrodes in Li/Seawater batteries; in this example the Li/Seawater cell is used in a sonobuoy; as can be seen in the above projection, the specific energy for Li/Seawater systems can be exceedingly high.